TEM structural analysis of photocatalytically active mesoporous single crystalline LaTiO2N particles

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Background incl. aims

Single crystalline mesoporous oxynitride particles have been studied as prospective catalysts in solar hydrogen-generating devices [1]. Both, photocatalytic and photoelectrochemical applications benefit from the high active surface area of catalytic particles in combination with good charge-transport properties [2]. A suitable combination of desired properties is achieved in the case of large mesoporous LaTiO2N single crystalline particles (up to 1 µm). The absence of grain boundaries reduces charge carrier recombination while at the same time their porosity results in increased surface area [3][4]. LaTiO2N mesoporous particles are obtained by transforming La2Ti2O7 particles in a thermal ammonolysis process. In this contribution, we focus on a structural description of pore formation and pore arrangement concerning the LaTiO2N orthorhombic lattice.

Methods

The photocatalytically active mesoporous single-crystalline LaTiO2N particles were synthesised via a thermal ammonolysis process La2Ti2O7 + 2 NH3 ⇌ 2 LaTiO2N + 3 H2O, T > 900 °C.

A dual beam microscope Thermo Fisher Scientific Helios 5 FX was used for SEM imaging (immersion mode, in-lens detector, 3 kV, 100 pA) and orientation-specific preparation of electron transparent samples. Chunks of mesoporous particles were lifted out and transferred onto a compustage holder. The thinning was performed at ion accelerating voltage ranging from 30 to 2 kV and beam current ranging from 2 nA to 25 pA. During the thinning process, the sample was aligned using α and β tilts of the compustage holder in combination with a pixilated 4D STEM detector.

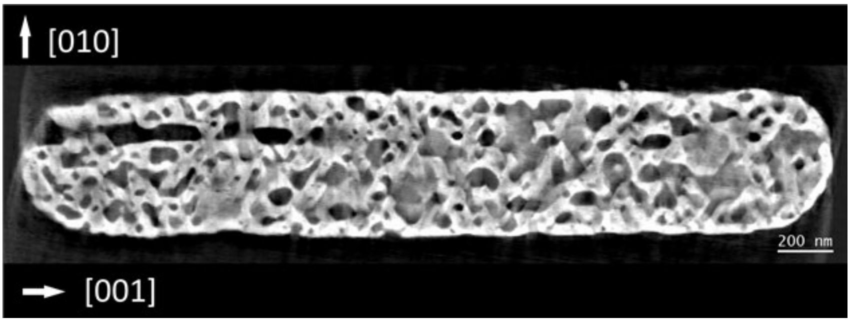
TEM/STEM analyses were performed using a JEOL F200 cold FEG microscope operated at an accelerating voltage of 200 kV. For the STEM-EELS analyses, CEOS CEFID energy filter equipped with a Tvips XF 416 CMOS camera was used. Tomograms were obtained by performing tilt series with a step width of 2° from −54° to 78° in STEM HAADF mode. For tomography, a 200 mesh copper grid coated with a continuous carbon thin film (Plano GmbH) was used. The 3D reconstruction was carried out with ImageJ and the 3D representation with the Amira software (Thermo Fisher Scientific).

Results

The topotactic thermal ammonolysis process conserves the overall size of the particles while at the same time creating a network of both closed and opened pores. Closed volume porosity was estimated to 12% based on a STEM tomography reconstruction. The orientation and arrangement of the pores were compared to the orientation of the crystal. TEM images in combination with SAD patterns show long axes of the pores (ranging from 20-60 nm) oriented along the [001] and [010] directions of the orthorhombic LaTiO2N Imma structure (ICSD-168551). The EELS data was recorded over closed pores and the surrounding matrix. The nitrogen K-eddge (402 eV) shows a higher content of nitrogen in the closed pores. This suggests the presence of entrapped nitrogen gas in the mesoporous structure.

Conclusion
Micrometer-sized mesoporous LaTiO2N particles were prepared by an ammonolysis process from La2Ti2O7 particles. The structural arrangement of the pores was analysed using TEM and STEM tomography techniques. The pores have their long axes oriented along the [001] and [010] lattice directions. The closed pores have a volume fraction of 12% and contain encapsulated nitrogen gas.

Graphic:



Keywords:

TEM, 2N, Mesoporous, Photocatalysis

Reference:

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