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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Probing local and long-range structure of N-doped TiO_2-based composite (TiO_2, Sn/SnO_2) materials for advanced photo-electrochemical applications	**Experiment number**: MA-3713
Beamline: BM-08	**Date of experiment**: from: 03 May 2018 to: 07 May 2018	**Date of report**:
Shifts: 12	**Local contact(s)**: Giovanni Orazio LEPORE	*Received at ESRF:*

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Report:

This work focuses on TiO_2:Sn and TiO_2:N,Sn nanostructured powders for advanced photo-electrochemical applications. A total of 16 samples were analyzed by XAS techniques (XANES/EXAFS) at the Ti K-edge, Sn L_1- and Sn K-edges at the LISA beamline (BM08). This set of results complements high-resolution X-ray powder diffraction patterns that were collected at the ID-22 beamline in January.

Analyzed samples. Both pristine, N-doped and N,Sn-copromoted TiO_2 samples were analyzed (Tab.1). Three different synthetic approaches were compared for the preparation of TiO_2:N,Sn systems: the mechanical mixing of a titania xerogel and nanosized hydrothermal SnO_2; the seeded growth of TiO_2 using crystalline SnO_2 germs; a sol-gel approach using both titanium alkoxide and a Sn salt as precursors (bulk approach). All of the prepared samples were finally calcined at 400°C in oxygen flux. Commercial and *ad hoc* synthesized TiO_2 and SnO_2 samples were also analyzed as references.

Table 1. List of performed analyses.

sample name	synthetic procedure	N-doping	Sn/Ti mol ratio	Ti K-edge	Sn K-edge	Sn L_1-edge	*operando* Ti K-edge	*operando* Sn L_1-edge
SnO_2com	Commercial	-	Pure SnO_2		X			
SnO_2	Hydroth+calc	X	Pure SnO_2		X	X		X
Ti	Sol-gel	-	Pure TiO_2	X				
TiN	Sol-gel	X	Pure TiO_2	X			X	
MSn10	Mech. mixing	-	10%	X	X			
MNSn10	Mech. mixing	X	10%	X	X			
MNSn20	Mech. mixing	X	20%	X	X	X	X	X
BSn10	Bulk synth.	-	10%	X	X			
BNSn3	Bulk synth.	X	3%	X	X			
BNSn5	Bulk synth.	X	5%	X	X			

BNSn10	Bulk synth.	X	10%	X	X		X	X
BNSn20	Bulk synth.	X	20%	X	X	X	X	X
SSn10	Seeded gr.	-	10%	X	X			
SNSn3	Seeded gr.	X	3%		X			
SNSn10	Seeded gr.	X	10%	X	X			
SNSn20	Seeded gr.	X	20%	X	X	X	X	X

Experimental details. X-ray absorption curves were collected around both Ti K-edge, Sn L_1- and K-edges at room temperature in He atmosphere at 1 atm. Spectra were recorded in transmission mode after diluting (when necessary) the powder in cellulose to avoid thickness effects. Fluorescence spectra could not be collected due to experimental problems with the detector. A Si (111)-monochromated beam was employed in the 4.87-5.71 (Ti K-edge), 4.39-4.85 (Sn L_1-edge) and 29.0-29.9 keV (Sn K-edge) energy ranges. Ti foil and Sn foil were analyzed as references for Ti and Sn K-edge spectra. Selected samples were analyzed also under *in situ* irradiation with a UV halogenide lamp (Jelosil HG 500 W). The Horae suite of programs, based on the IFEFFIT library, was used throughout data processing and fitting.

Main results. In the Sn-containing samples from the bulk series, the edge energy, E_0, of Sn L_1-edge spectra is slightly shifted (+2 eV) toward higher energies with respect to the reference SnO_2 (Fig. 1a). Moreover, the near-edge features above the white line show a different Sn coordination geometry with respect to the pure SnO_2 reference. The other two series present Sn L_1-edge spectra comparable to the reference pure cassiterite. Slight changes in the Sn L_1-edge spectra were observed upon UV irradiation which could be attributed to a partial reduction of Sn centres.
The Ti K-edge EXAFS spectra are mainly influenced, as expected, by the different phase composition of the samples, in terms of anatase and rutile content (Fig. 1b). The results of preliminary least-squares fittings shows that the bulk series presents appreciable distortions in the first coordination shell as a function of the Sn content (Fig. 1c), which are instead scarcely appreciable in the mechanical mixing and seeded growth series. Nitrogen has instead just immaterial effects, confirming previous considerations made on the basis of HR-XRPD data. Also UV irradiation has no effect on the average Ti geometry.
The Sn K-edge spectra of bulk samples display almost unchanged average $<d_{Sn-O}>$ distances in the anatase matrix at low Sn loadings, while they undergo an abrupt shortening at higher ones. This is consistent with an increase of the average oxidation state of Sn ion.

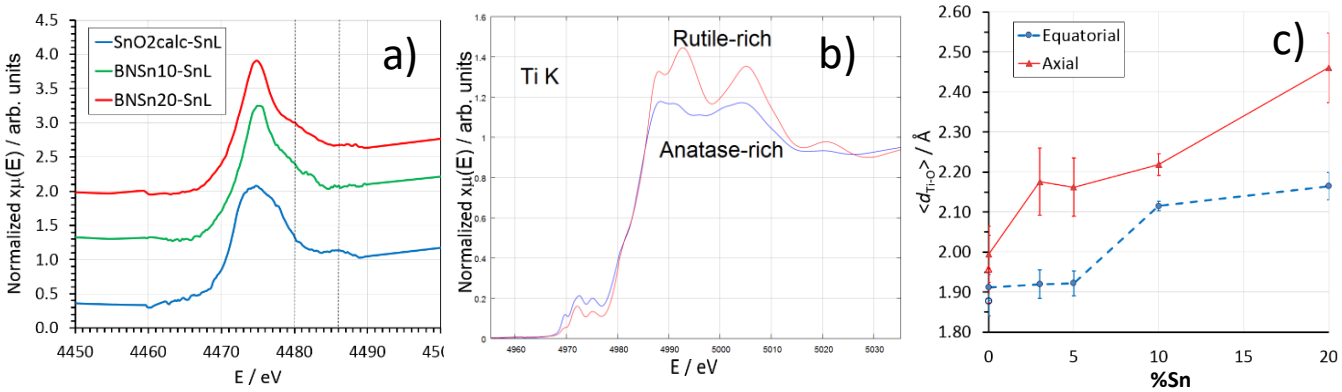

Figure 1. a) XAS signals across the Sn L_1 absorption edge for bulk series samples and the reference SnO_2; b) Ti K-edge signal in anatase rich and rutile-rich samples; c) EXAFS least-squares estimates of average $<d_{Ti-O}>$ distances for the first coordination shell of Ti as a function of the Sn content for the bulk sample series.

In conclusion, the present experiment complemented and supported the outcomes of the experimental session at ID22. We demonstrated that the adopted synthetic strategies are able to control the microstructure in terms of both phase composition and concentration of defects, which in turn imply significant changes in both the long- and short-range structures. Furthermore, the *operando* measurements provided evidence of electron transfer mechanisms taking place upon UV light irradiation. We are currently developing an interpretative framework to correlate these structural and microstructural insights to the observed optical and electronic properties.