EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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: ID-22	**Date of experiment**: from: 24/01/2018 to: 25/01/2018	**Date of report**: 13/02/2018
Shifts: 3	**Local contact(s)**: Mauro CODURI	*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. In the first part of the experiment, high-resolution X-ray powder diffraction patterns of a total of 22 samples were collected at the ID-22 beamline. This set of results will be complemented by XAS (XANES/EXAFS) data at the Sn L1 and Sn K edges, which will be collected at the LISA beamline (BM08) at a later date; the beamtime at LISA was postponed due to delays in the refurbishing of the beamline and was not yet rescheduled.

Analyzed samples. Both pristine, N-doped and N,Sn-copromoted TiO_2 samples were analyzed (Table 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.

#	sample name	synthetic procedure	N-doping	Sn/Ti molar ratio
1	SnO_2 comm	Commercial	-	Pure SnO_2
2	SnO_2 nc	Hydrothermal	X	Pure SnO_2
3	SnO_2	Hydrothermal + calcination	X	Pure SnO_2
4	TiO_2 rutile	Commercial	-	Pure TiO_2
5	TiO_2 anatase	Commercial	-	Pure TiO_2
6	Ti	Sol-gel	-	Pure TiO_2
7	TiN	Sol-gel	X	Pure TiO_2
8	MSn10	Mechanical mixing	-	10%
9	MNSn3	Mechanical mixing	X	3%
10	MNSn5	Mechanical mixing	X	5%
11	MNSn10	Mechanical mixing	X	10%
12	MNSn20	Mechanical mixing	X	20%

13	BSn10	Bulk synthesis	-	10%
14	BNSn3	Bulk synthesis	X	3%
15	BNSn5	Bulk synthesis	X	5%
16	BNSn10	Bulk synthesis	X	10%
17	BNSn20	Bulk synthesis	X	20%
18	SSn10	Seeded growth	-	10%
19	SNSn3	Seeded growth	X	3%
20	SNSn5	Seeded growth	X	5%
21	SNSn10	Seeded growth	X	10%
22	SNSn20	Seeded growth	X	20%

Table 1. List of the analyzed samples.

X-ray powder diffraction data were collected at RT from 3° to 48° in 2ϑ in Debye-Scherrer capillary geometry using Si-111 monochromatized X-rays at 29 keV. A multianalyzer stage with nine Si(111) analyzer crystals was employed throughout. Each diffraction pattern was thus obtained from the weighted average of the signals recorded by each module of the detector array. The X-rays wavelength, the offsets of each channel and the corresponding efficiency were calibrated using the NIST 640c Si standard. The Rietveld method was exlpoited to fit experimental diffractograms thorugh the GSAS program as implemented in the EXPGUI package. Selected samples were measured also under *in situ* irradiation with UV light from a portable UV torch. Long acquisitions were also carried out on the pristine SnO_2 specimens, characterized by a low crystallinity degree, in order to carry out pair distribution function (PDF) analyses.

Main results. Most of the TiO_2 samples are composed of anatase ($I4_1$/amd) as main phase and of a small amount of brookite (*P*bca), whose specific signature is the (211) reflection at ≈ 8.4 deg (Figure 1a). The different synthetic procedures exert a notable influence on the structural properties of the samples. In particular, in the bulk series, the Sn addition promotes the formation of rutile TiO_2 ($P4_2$/mnm), as appreciable from the peak at ca. 7.5 deg, at the expenses of the other TiO_2 polymorphs. Moreover, for this series, segregated cassiterite SnO_2 ($P4_2$/mnm, signature peak at *ca.* 9.2 deg) cannot be appreciated even at high Sn content. On the other hand, a rutile promotion effect is not observed for the seeded growth and mechanical mixing series, where instead cassiterite SnO_2 is clearly appreciable. The main difference between the two latter series is related to the SnO_2 content, which in one case is compatible with the nominal amount, whereas in the seeded growth accounts for a small part of the nominal content. In this respect, the structure of the nanosized SnO_2 germs adopted in both synthetic routes was investigated via PDF analyses (Figure 1b). In addition, XAS experiments will integrate this picture, providing information about the location of the Sn and N species, especially for the samples where no segregated SnO_2 phases are appreciable.

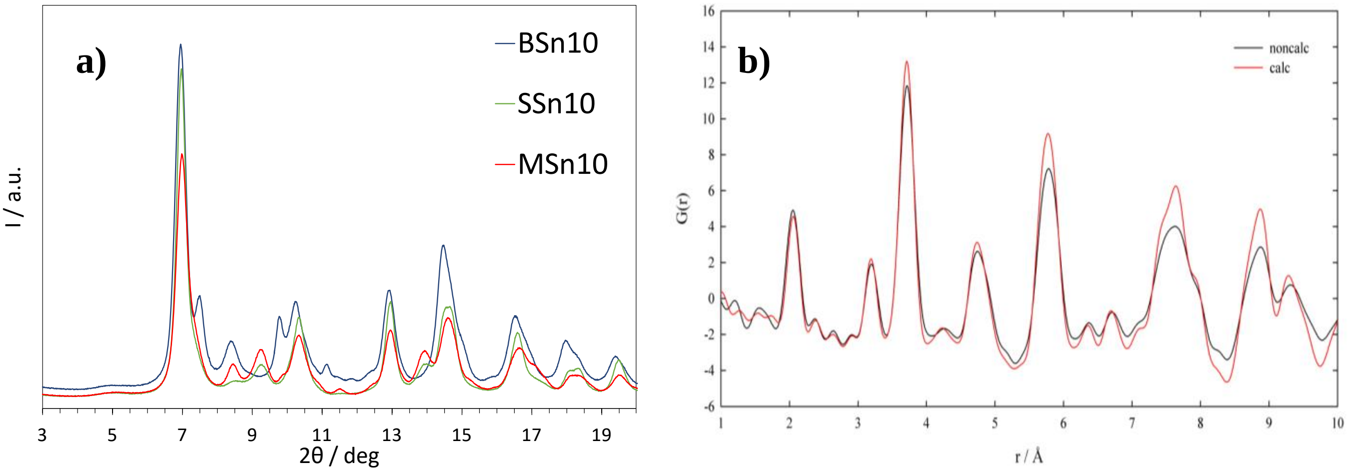

Figure 1. (a) XRD patterns of TiO_2:Sn,N samples prepared by different synthetic procedures; (b) Experimental PDF data at short range for SnO_2 samples before (black curve) and after calcination (red curve).