



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://www.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.

**Experiment title:**

Nature of defects in titania nanostructures

Experiment**number:**

25-01-971

Beamline:**Date of experiment:**

from: 25.11.2015 to: 28.11.2015

Date of report:**Shifts:****Local contact(s):**

Eduardo Salas-Colera

*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):**

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Report:

The experimental goal was to establish the effect of the presence of N- and O-interstitial dopants on the local structure of Ti in anatase titanium dioxide photocatalysts. The samples of TiO₂ were previously synthesized in the Lab of University of Oviedo by three different procedures using titanium oxysulfate and titanium peroxy complex as precursors and ammonia as a source of nitrogen. The titania samples containing N-dopants were obtained at heat treatment temperatures of 400 and 500 °C and marked as T_400 and T_500. Oxygen doped titania was obtained at higher temperatures of 600 and 800 °C and these samples were designated as T_600 and T_800 (Fig. 1).

X-ray absorption data were collected around Ti K-edge using a -70 °C ethanol cooled double Si(111) crystal, which gave an energy resolution of $\Delta E/E = 1.5 \times 10^{-4}$. The experiment was performed at room temperature in fluorescence mode at standard 45° geometry. For fluorescence detection, Sirius liquid nitrogen cooled multi-element solid state X-Ray detector from e2v was employed. The detector included 13 Si(Li) crystal sensors mounted on a low noise electrically restored FETs. Pure commercial TiO₂ anatase (Aldrich), the nitrogen-doped and the oxygen-rich samples were measured in the energy range from 4.8 to 5.7 keV.

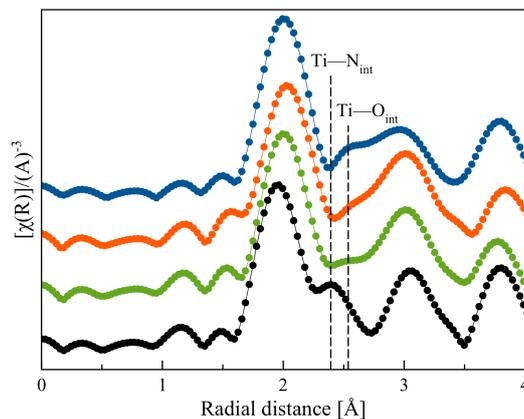


Figure 1. The representative EXAFS data for a series of titania samples. Extended region fitting using ARTEMIS in R-space for (—) T_400, (—) T_500, (—) T_600, and (—) T_800 samples

Table 1. The results of EXAFS data fitting.

Sample	Path	Coordination number	R [Å]	σ^2 [Å ²]
T_400	Ti-O equatorial	3.46 (2)	1.935 (2)	0.0003 (1)
	Ti-O axial	1.58 (2)	1.977 (2)	0.0003 (1)
	Ti-N_interstitial	0.99(6)	2.436 (4)	0.0004 (1)
	Ti-Ti	3.62 (2)	3.033 (1)	0.002 (1)
T_500	Ti-O equatorial	3.21 (2)	1.959 (2)	0.0003 (1)
	Ti-O axial	1.65(2)	1.975 (3)	0.0003 (1)
	Ti-N_interstitial	0.45(6)	2.352 (2)	0.0001 (1)
	Ti-O_interstitial	0.51(7)	2.581 (4)	0.002 (1)
	Ti-Ti	4.26(2)	3.035 (1)	0.002 (1)
T_600	Ti-O equatorial	3.36 (2)	1.968 (2)	0.0003 (1)
	Ti-O axial	1.89(4)	1.976 (2)	0.0003 (1)
	Ti-O_interstitial	1.05(8)	2.620 (7)	0.010 (2)
	Ti-Ti	4.03(3)	3.039 (3)	0.001 (1)
T_800	Ti-O equatorial	3.61(1)	1.961 (2)	0.0002 (1)
	Ti-O axial	2.25 (2)	1.973 (2)	0.0002 (1)
	Ti-O_interstitial	1.28 (9)	2.537 (5)	0.010 (1)
	Ti-Ti	4.41 (2)	3.026 (2)	0.004 (1)
Anatase (Aldrich)	Ti-O equatorial	4.00	1.939 (2)	0.0001 (1)
	Ti-O axial	2.00	1.976 (3)	0.0001 (1)
	Ti-Ti	4.00	3.042 (2)	0.0006 (1)

R – bond distance; σ – XAFS Debye-Waller factor

The obtained during the experiment results have allowed us reconsidering the mechanism of oxygen-rich titania formation from a precursor containing a source of nitrogen. We have demonstrated that at low temperatures of thermal treatment (400-500 °C) nitrogen-doping of TiO₂ anatase titania occurs, and the N-

species occupy interstitial position in the titanium dioxide anatase crystal structure causing creation of defects (oxygen vacancies) in the titanium first coordination shell. The treatment under air at high temperatures completely removes the N-dopants, thus leaving the Ti coordination unsatisfied provoking the charge imbalance in the TiO₅ units. It forces the neighbouring oxygen atoms to occupy a vacant place, which in its turn results in the cascade reaction of adsorption of atmospheric oxygen and its diffusion to the unoccupied sites. The captured oxygen forms the interstitial O-species inside the TiO₂ network, expanding the TiO₂ crystal cell. The coordination number of Ti in the oxygen-rich titania exceeds the value of 6, thus implying the formation of O-O peroxo bridges coordinating titanium atoms (Table 1).

[1] I. Krivtsov, M. Ilkaeva, E. Salas-Colera, Z. Amghouz, J.R. Garcia, E. Diaz, S. Ordoñez, S. Villar-Rodil, J. Phys. Chem. C, 2017, 121, 6770.