EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Surface plasmon resonance enhancement of photocatalytic activity in TiO2 nanostructures	**Experiment number**: HC-1263
Beamline:	**Date of experiment**: from: 26/02/2014 to: 04/03/2014	**Date of report**:
Shifts:	**Local contact(s)**: Jean Daniel Cafun	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

We investigated the interaction of TiO_2 powders and Au nanoparticles under the excitation of the surface plasmon resonance (SPR) of Au nanoparticles (NPs). We choose three TiO_2 powders: white TiO_2, which is stoichiometric, black TiO_2, which is rich of oxygen vacancies and N-doped TiO_2. After the static characterization we looked for changes of the Ti K-edge induced by the excitation of the SPR of Au NPs. We used a CW laser of 532 nm to excite the Au NPs. The power used was 200 mW on a laser spot of almost 1.5 mm diameter. We acquired TFY XANES and HERFD at two emission energies, HERFD-I at Kbeta maximum and HERFD-II at a lower emission energy to better resolve pre-edge peaks due to more localised orbitals, alternating laser on and laser off acquisitions by using a shutter to block the laser.

We observed relevant spectral differences between laser on – laser off spectra on all three samples, pointing out to the same effect which can not depend on doping. Analysis of spectral variations indicate a twofold behaviour: HERFD-I is red-shifted by the laser while spectral features in HERFD-II undergo a change in spectral weight. HERFD-I is sensitive to more delocalised p-orbitals while HERFD-II to more localised d-orbitals. This twofold behaviour is thus due to electrons injected from Au NPs to TiO2 which remain trapped in p-orbitals around distorted Ti sites at the surface. By using continuous irradiation we are sensitive to long-lived charges, the one which can survive enough to participate to catalysis at the surface.
A paper based on results obtained during this beamtime has been recentrly accepted on Angewandte Chemie International Edition.

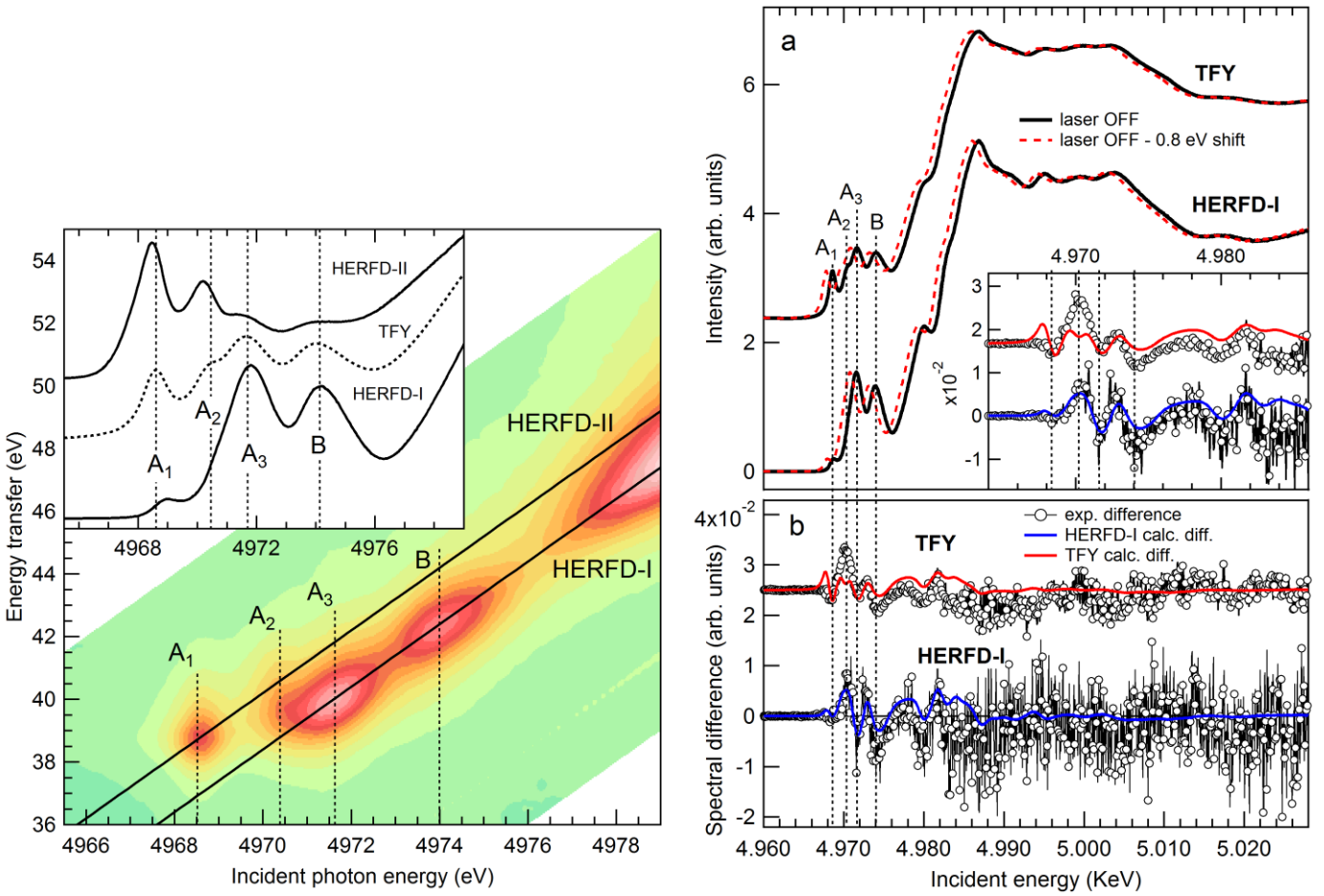

Figure 1: Left: RIXS plane of Ndoped TiO_2 pre-edge, showing the RIXS cut acquired separatly to see the laser effect on different spectral features. The inset shows HERD-I, TFY and HERFD-II Ti pre-edge. Right: a) full HERFD-I and TFY XANES on N-doped TiO2 and the red-shifted spectrum (-0.8 eV) used to reproduce the laser effect. b) experimental laser on – laser off differences compared with shifted – unshifted differences for HERFD-I and TFY. Enhancement of the pre-edge is shown in the inset of a).