



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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now 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: Structure of Acetate adsorbed on TiO ₂ (110) as a function of pH	Experiment number: SI 2085
Beamline: ID32	Date of experiment: from: 14/04/2010 to: 27/04/2010	Date of report: 28/02/2011
Shifts: 18	Local contact(s): Blanka Detlefs	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

G. Thornton* , H. Hussain*

Chemistry Department and LCN, University College London, UK

R. Lindsay*

Corrosion and Protection Centre, University of Manchester, UK

X. Torrelles*

Institut de Ciència de Materials de Barcelona (CSIC), Spain

G. Cabailh*

Institut des Nanosciences, CNRS, Paris, France

O. Bikondoa*

Physics Department, University of Warwick, UK

Report:

The adsorption and surface reactivity of simple carboxylates (*e.g.* formate and acetate) on the TiO₂(110) have been extensively investigated in *UHV* [1]. In part, interest lies in the use of these species as mimics for dye molecules employed in Grätzel-type dye sensitised solar cells, which are promising candidates for next generation photovoltaics. Grätzel's group have used attenuated total reflection – fourier transform infrared spectroscopy (ATR-FTIR) to study the adsorption of formate/acetate from *aqueous solution* at varying pHs (3 - 9) onto rutile TiO₂(110) [2]. Their experimental data indicate that formate/acetate ions are adsorbed in a bridge-bonded configuration, which is the same geometry as that found in *UHV* studies [3,4]. As regards coverage, a maximum was achieved at pH 4, with the pH being varied by adding HCl or NaOH [2]. We proposed to investigate the adsorption of acetate with SXR D as a function of pH, using dilution as well as the addition of a strong acid or base.

In this experiment we aimed to perform a quantitative structural determination of the interface between TiO₂(110)1x1 and acetate in aqueous solution as a function of pH, employing surface X-ray diffraction (*SXR D*). *In situ* substrate preparation was carried out in

UHV facilities located in the Surface Characterisation Laboratory (*SCL*) by repeated cycles of argon ion sputtering and annealing until a sharp 1×1 *LEED* pattern and characteristic STM images were obtained. The sample was then transferred under *UHV* to beam line *ID32*, using a *Baby* chamber configured for solid/liquid interface experiments [5]. *SXRD* measurements were performed on the diffractometer in *EHI*, employing a photon energy of 17.71 keV. Data were collected at room temperature using conventional rocking scans, in which the sample is rotated about its surface normal while scattered x-ray intensity is measured. For a given (h,k) these were performed at different l , enabling crystal truncation rods (*CTRs*) to be compiled. Prior to acetate exposure, 14 *CTRs* were acquired from the $\text{TiO}_2(110)1 \times 1/\text{UHV}$ interface, both to ensure sample integrity and to easily identify structural changes due to the presence of acetate. Acetate immersion was achieved using a capillary tube to deliver an acetate droplet onto the $\text{TiO}_2(110)1 \times 1$ surface, which had previously been exposed to an atmospheric pressure of N_2 .

After taking several measurements of acetate adsorbed on the $\text{TiO}_2(110)1 \times 1$ surface, a change in the hydrophobic nature of the acetate droplet was observed. Upon extraction of the capillary tube a brown staining of the sample and discolouration of the acetate was present. Contact angle experiments conducted at *The University of Manchester* and at the *ESRF* concluded that this discolouration does not naturally occur but can be ascribed to beam damage of the liquid. Further tests conducted at *University College London* suggested that the acetate solution etched the Mo sample plate. Figure 1 displays the time evolution of the $[1,0,1.25]$ control reflection measured during the experiment. After 24 hours (inset) the intensity decreased almost 20 times from the beginning while the background intensity increased the same proportion (a factor 20).

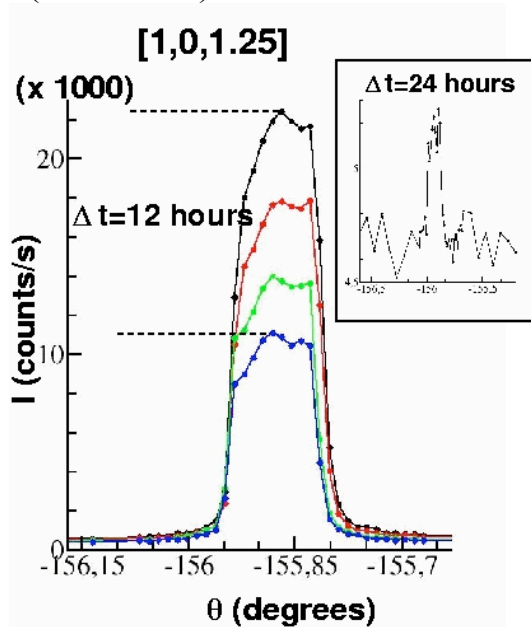


Figure 1: Time evolution of the $[1,0,1.25]$ reflection.

References

- [1] C.L. Pang *et al*, Chem. Soc. Rev. 37, 2328 (2008).
- [2] F.P. Rotzinger *et al*, J. Phys. Chem. B 108, 5004 (2004).
- [3] D.I. Sayago *et al*, J. Phys. Chem. B 108, 14316 (2004).
- [4] R. Lindsay *et al*, J. Phys. Chem. C 112, 14145 (2008).
- [5] www.esrf.fr/UsersAndScience/Experiments/SurfaceScience/ID32/SurfaceLab/