



## 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>

### Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

#### Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

### Deadlines for submitting a report supporting a new proposal

- 1<sup>st</sup> March Proposal Round - **5<sup>th</sup> March**
- 10<sup>th</sup> September Proposal Round - **13<sup>th</sup> September**

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.

### Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** Investigating oxidation state and stability of Ni and Cu co-catalysts on TiO<sub>2</sub> photocatalyst for H<sub>2</sub> evolution by *in-situ* X-ray Absorption Spectroscopy

**Experiment number:**  
CH6517

<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 20/09/2022 to: 26/09/2022	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b>	<b>Local contact(s):</b> Viktoriia Saveleva	

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**Report:**

**1. Aim and methodology**

The present work investigates compositional changes of Ni, Cu, and NiCu co-catalysts on a TiO<sub>2</sub> photocatalyst for H<sub>2</sub> evolution under transient UV illumination. For this, we performed *in-situ* XAS measurements in fluorescence mode on 10 nm-thick nanocrystalline Ni, Cu, and NiCu co-catalyst thin films on ~8 μm-thick mesoporous TiO<sub>2</sub> layers. Experiments were conducted in de-ionized H<sub>2</sub>O and H<sub>2</sub>O/MeOH (20 vol%) solutions, under intermittent illumination conditions (*i.e.*, light on/off cycles). The summary of the experiments is shown in Table 1.

Table 1. Summary of experiments

Experiment	Catalyst	Solution	Illumination sequence
Ni_H <sub>2</sub> O	Ni_TiO <sub>2</sub>	H <sub>2</sub> O	Dark1 → UV → dark2
Cu_H <sub>2</sub> O	Cu_TiO <sub>2</sub>	H <sub>2</sub> O	Dark1 → UV → dark2
NiCu_H <sub>2</sub> O	NiCu_TiO <sub>2</sub>	H <sub>2</sub> O	Dark1 → UV → dark2 → UV2 → dark3
Ni_MeOH	Ni_TiO <sub>2</sub>	20 vol% MeOH/H <sub>2</sub> O	Dark1 → UV → dark2
Cu_MeOH	Cu_TiO <sub>2</sub>	20 vol% MeOH/H <sub>2</sub> O	Dark1 → UV → dark2 → UV2
NiCu_MeOH	NiCu_TiO <sub>2</sub>	20 vol% MeOH/H <sub>2</sub> O	Dark1 → UV → dark2 → UV2

For the *in-situ* measurements, we adapted a homemade cell (as sketched in Figure 1a) that we used in our previous work<sup>[1]</sup>. To grant transparency to both X-ray and UV light, a Mylar window was used. We used a UV LED light source emitting at 365 nm with a power density of ca. 100 mW/cm<sup>2</sup>. The co-catalyst oxidation state was probed by time-resolved X-ray fluorescence spectroscopy, by acquiring Ni and Cu K-edge XANES spectra. To improve the signal-to-noise ratio, groups of 20 scans were merged and then fitted using the software Athena. This provides a time resolution of *ca.* 30 minutes. To minimize beam damage, a beam size of 200 μm × 400 μm

was chosen and a scanning pattern was created to acquire each spectrum at a previously unexposed location. To minimize sample exposure to the X-ray beam, the fast shutter was kept always closed except during data acquisition.

## 2. Results and discussion

Before starting the *in-situ* experiments, references were measured to perform linear combination fitting. Said references were: 100 nm thick sputter-deposited films on SiO<sub>2</sub> wafer, and powders of NiO, Cu<sub>2</sub>O and CuO. The obtained spectra presented severe spectral distortion caused by self-absorption. For this reason, we disregarded such reference spectra and fitted the XANES spectra using reference spectra obtained in transmission mode in previous beam times (*e.g.*, at DESY, Hamburg, Germany). Such reference spectra used for fitting were obtained for metallic Ni and Cu foils, powders of NiO, Ni(OH)<sub>2</sub>, Cu<sub>2</sub>O and CuO, and aqueous NiSO<sub>4</sub> solution.

We discuss in the present report only data for experiment “Ni\_H<sub>2</sub>O” for the sake of brevity.

**Ni\_H<sub>2</sub>O:** Figure 1b shows the trend of atomic fraction over time for different Ni phases obtained by fitting the *in-situ* XANES spectra for experiment “Ni\_H<sub>2</sub>O”. Due to the similarity between XANES spectra of NiO and Ni(OH)<sub>2</sub>, the sum of their fractions is plotted as Ni<sup>2+</sup> (solid) for ease of interpretation. The as-prepared sample was analyzed *ex-situ*. The XANES data indicate that the as-prepared co-catalyst (time = 0 min) is composed of metallic and oxidized Ni (NiO/Ni(OH)<sub>2</sub>) with a ratio of 1:1. The co-catalyst oxidization might be caused by i) air exposure, and/or ii) O<sub>2</sub> uptake during the sputtering procedure. After immersing the Ni-TiO<sub>2</sub> photocatalyst in de-ionized H<sub>2</sub>O in the *in-situ* cell, a slight decrease in the atomic fraction of Ni<sup>2+</sup> can be observed in the first 18 minutes. This composition change can be explained considering the dissolution of the surface oxide layer. The system then proves to be stable over time (up to 136 minutes after immersion), as no further change in the oxidation state of the co-catalyst film can be observed.

UV1: More remarkable changes, however, occur during UV illumination (“UV” in Figure 1b): after approximately 40 minutes of UV light irradiation, the Ni co-catalyst layers starts to oxidize rapidly and no metallic Ni can be detected after 100 minutes of UV irradiation. At the same time, the formation of aqueous Ni<sup>2+</sup> can be observed. These results indicate oxidation of the Ni co-catalyst followed by dissolution of oxidized Ni species. This is consistent with what was observed by Crozier *et al.*<sup>[21]</sup>, who suggested that metallic Ni is oxidized by hydroxyl radical (OH·, formed by photogenerated holes, see below Eq. 5) and then dissolved in H<sub>2</sub>O.

Dark2: After switching off the UV illumination (“dark2” in Figure 1b), no Ni<sup>2+</sup> ions can be probed, and the results of fitting indicate that Ni is fully oxidized and present as solid Ni<sup>2+</sup> species, likely in the form of a mixture of NiO and Ni(OH)<sub>2</sub> (solid) phases. This might be due to a dynamic equilibrium between the oxidized layer dissolution and the ions diffusion from the probed area. Note that the beam size is 0.08 mm<sup>2</sup>, *i.e.*, the probed volume of aqueous solution is small, and once Ni<sup>2+</sup> ions are no longer formed, they might diffuse towards the solution bulk. In other words, once the UV light is turned off, the Ni oxidation/dissolution ceases, which causes the concentration of solvated Ni<sup>2+</sup> ions in the probed volume to decrease below the detection limit, due to ion diffusion towards the solution bulk. Other characterization techniques, *e.g.*, SEM, XPS, ICP-MS, *etc.*, along with online GC measurements to evaluate the kinetics of H<sub>2</sub> evolution, are required to validate this interpretation.

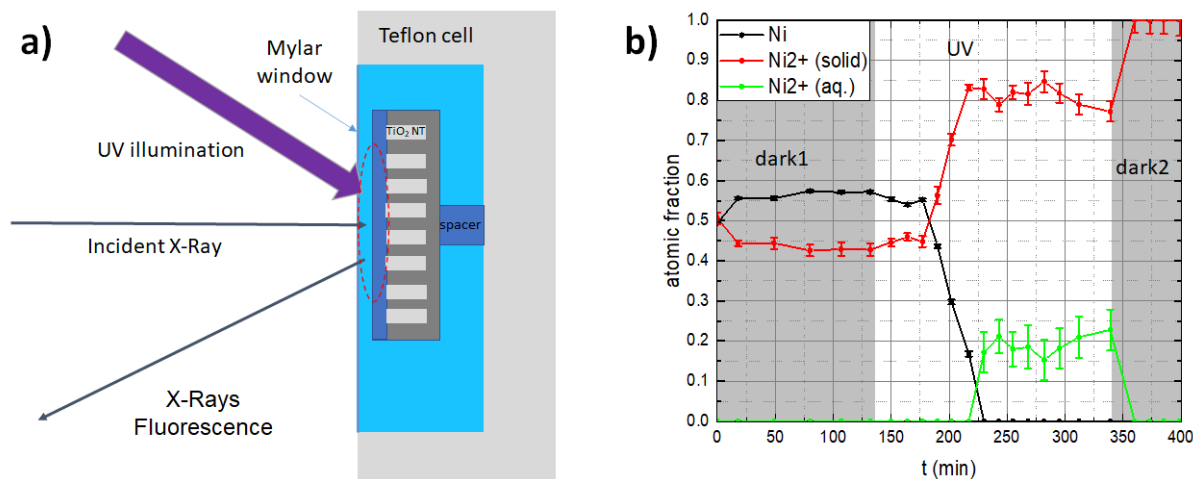
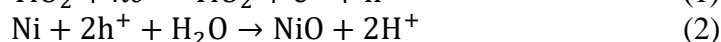
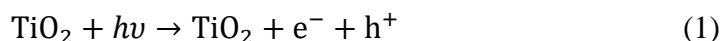


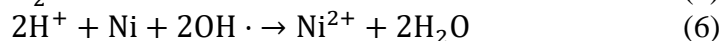
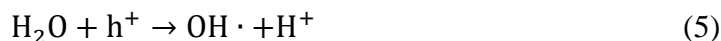
Figure 1. a) sketch of the *in-situ* XAS cell; the red ellipse indicates the region of interest, i.e., the co-catalyst film and the thin liquid film between the sample and the Mylar window; b) linear combination fitting results of XANES spectra of experiment Ni<sub>2</sub>O<sub>3</sub>.

### 3. Conclusion

The obtained data allow for following *in-situ* the behavior of nanocrystalline Ni co-catalytic thin films on mesoporous TiO<sub>2</sub> in pure water. Summarizing, no significant changes occur in the Ni co-catalyst without UV illumination. However, irradiation with UV light causes the complete oxidation of the co-catalyst thin film and its partial dissolution according to the following reaction scheme (Equations 1-3):



To the best of our knowledge, our results provide the first experimental *in-situ* evidence to corroborate the observation of Crozier *et al.*<sup>[2]</sup> who observed Ni oxidation and dissolution by performing *ex-situ* ICP-MS measurements, and proposed the following mechanism (Eq. 5-6), consequent to Eq. 1-3:



We plan to complement the obtained XAS data with results from *ex-situ* analytical techniques (*e.g.*, XPS, ICP-MS, *etc.*) and of photocatalytic experiments combined with online head space analysis by gas chromatography (GC). The same will be done for Cu and NiCu modified TiO<sub>2</sub> photocatalysts.

### 4. References

- [1] D. Spanu, A. Minguzzi, S. Recchia, F. Shahvardanfard, O. Tomanec, R. Zboril, P. Schmuki, P. Ghigna, M. Altomare, *ACS Catal.* **2020**, *10*, 8293–8302.
- [2] L. Zhang, Q. Liu, T. Aoki, P. A. Crozier, *J. Phys. Chem. C* **2015**, *119*, 7207–7214.