

EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

Hyperfine interactions in hydrogenated TiO₂ thin films and powders for photocatalytic reactions

[January 8th 2018]

Dmitry Zyabkin¹, Juliana Schell^{2,3}, Doru C. Lupascu³, Haraldur Pall Gunnlaugson⁴, Hilary Masenda⁵, Roberto Mantovan⁶, Krish-Baruth-Ram^{7,8}, Sveinn Ólafsson⁹, Hafliði P. Gíslason⁹, BingCui Qi⁹, Petko Rkastev¹⁰, Joao Guilherme Martins Correia^{2,11}, Ulrich Vetter¹, Peter Schaafi

1 Department of Materials for Electronics, Institute of Materials Science and Engineering, TU Ilmenau, Gustav-Kirchhoff-Strasse 5, 98693 Ilmenau, Germany

2 EP Department, ISOLDE-CERN, CH-1211 Geneva 23, Switzerland

3 Institute for Materials Science and Centre for Nanointegration, Duisburg-Essen (CENIDE),

4 Science Institute, University of Iceland, Dunhaga

5 School of Physics, University of the Witwatersrand, Johannesburg, 2050, South Africa

6 Laboratorio MDM, IMM-CNR, Via Olivetti 2, 20864, Agrate Brianza (MB), Italy

7 Durban University of Technology, Durban, 4000, South Africa.

8 School of Chemistry and Physics, University of KwaZulu-Natal, Durban, 4000, South Africa

9 Science Institute University of Iceland

10 Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences, 72, Tsarigradsko Chaussee Boulevard, Sofia, 1784, Bulgaria

11 Centro de Ciências e Tecnologias Nucleares (CCTN), Instituto Superior Técnico, Universidade de Lisboa, Portugal

Spokesperson(s): Dmitry Zyabkin, Juliana Schell
Local contact: Juliana Schell (Juliana.Schell@cern.ch)

Abstract

TiO₂ is one of the most promising materials nowadays for photo catalytic applications. With the help of additional hydrogenation its catalytic efficiency can be significantly improved. It was observed that it was the near-surface defects induced by the “mild” hydrogenation of the TiO₂:H that play the key role in improving the photocatalytic process. Therefore, understanding the defect formation phenomena on a local atomic level is most desirable and an essential step towards realizing a stable, catalytic efficiency of the system through systematic defect engineering. Our project aims to take advantage of the local atomic probing strengths of Mössbauer spectroscopy and Time Dependent $\gamma\gamma$ -Angular Correlation Spectroscopy, to investigate the local defects in the nanostructured TiO₂:H thin films at the atomic scale and to correlate our results with the photo catalytic efficiency of hydrogenated TiO₂. The defects to be investigated would be systematically controlled by the thin film preparation parameters, such as synthesis and post-hydrogen plasma treatment temperatures, as well as in-situ measurement temperatures and light-irradiation conditions. From the results we expect important



insight into the hydrogenation enhanced catalytic processes and input for future TiO₂:H preparation routes.

Requested shifts: 7 shifts, (split into 3(4) runs over 1 year)

Introduction and motivation

In order to retain our innovation strength and guarantee a safe sustainable energy supply, photocatalytic materials play an increasing role for the world. The energy turnaround can only be successful if the necessary materials and technologies can be developed [EU14]. Photocatalysis, for instance, can significantly improve the splitting of water, more efficiently catalyse CO₂ with water to methane, or support the cleaning and conditioning of water with sun light [NI07].

A photocatalytic (PC) cell uses solid-state electrodes in a similar way to conventional electrolyzers, where H₂O oxidation (or O₂ evolution reaction) and reduction (H₂ evolution reaction) take place at two different solid/liquid junctions. In PC cells, one of the electrodes consists of a semiconductor capable of absorbing the incoming light, and in which a depletion (or space-charge, SC) region is formed at equilibrium.

A schematic description of the photocatalytic process is shown in figure 1, where inside the photocatalytic material free charge carriers are generated by (sun) light and are then further involved in oxidation or reduction processes. If recombination takes place too fast, or if the free energy carriers cannot migrate to the electrodes, then the efficiency of the photocatalytic process drops.

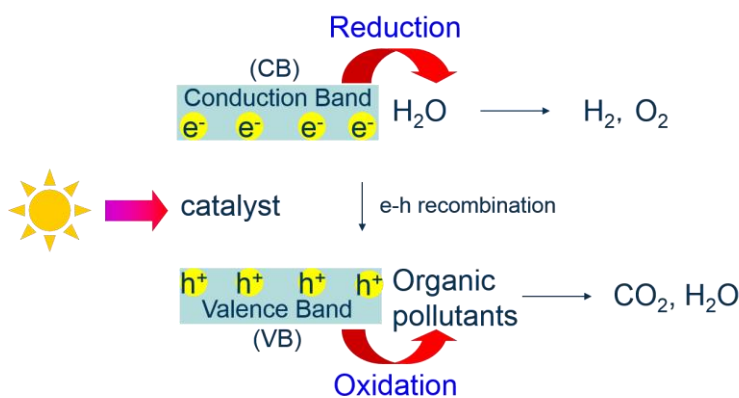


Figure 1: Schematic description of the photocatalytic process (after Ref. [YAN15]).

The photo-generated electrons and holes may recombine inside the electrode material or at its surface and so release energy in the form of photons or heat. Only those free charge carriers that reach the surface can contribute to the photocatalytic process since they come into contact with the reactants. This makes nanomaterials the preferable choice due to the larger surface to volume ratio. Implantation of additional metal atoms (Pt, Au, Pd, Rh, Ni, Cu, Ag, Zn, Fe, etc.) has proven to be quite useful in enhancing the materials efficiency [NI07]. Since many of these elements have isotopes that can be investigated by means of Mössbauer spectroscopy or time differential γ - γ angular correlation spectroscopy (TDPAC, see Ref. [SCH17B]) such nuclear probes are promising for studying directly the effects of the dopant ions on the photo catalysis and contributing to an understanding of the underlying mechanisms in such

materials like e.g. TiO_2 , ZnO or Fe_2O_3 . Especially, charge carrier separation and the carriers further evolution in the material play an important role.

Regarding the fabrication and investigation of photocatalytic materials we have performed numerous investigations during the past years, with a focus on TiO_2 [YAN13, IVA14, YA14A, YA14B, REN15, PJE15, WAN15]. We have developed a "mild" plasma treatment facility, which allows to adjusting a defined defect structure in TiO_2 , thereby modifying and improving optical and photocatalytic effects significantly. Such changes can be clearly seen in colour and absorption spectra, while in TEM measurements only surface, but not bulk, effects are observed [YAN14B].

Figure 2 presents the generation rate of CH_4 and CO due to the photocatalytic reduction of CO_2 with H_2O by $\text{H-TiO}_2:\text{H}_2$ for different plasma treatment times. It clearly shows that plasma-induced defects have a positive impact on methane synthesis. However, an abundance of defects reduces the efficiency of this process due to recombination of charge carriers, a process which is reflected by a rise in temperature.

In order to understand these processes on an atomic scale, i.e. to understand the nature of the H-related defects responsible for the quality of the material, we would like to make use of the local probing strength of ^{57}Fe -emission Mössbauer spectroscopy as well as TDPAC, which has already been demonstrated for co-doped TiO_2 (see eg. Refs. [GUN14, GAN16, WAN16, SUN17]). The results of such studies are expected to yield important insights into the role of defects in photocatalytic efficiency and lead to the development of highly efficient photocatalytic materials through (so-called) defect engineering.

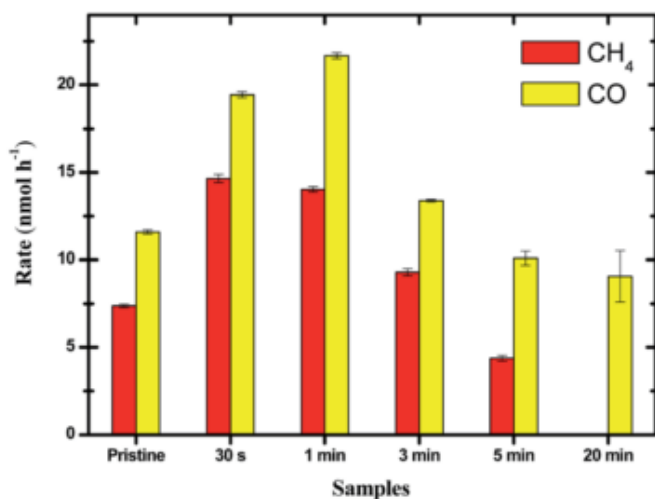


Figure 2: Generation rate of CH_4 and CO for the photo catalytic reduction of CO_2 with H_2O by $\text{H-TiO}_2:\text{H}_2$, plasma treated for different times of 30 s, 1 min, 3 min, 5 min, and 20 min [58].

There exist only a few studies of Mössbauer spectroscopy coupled with irradiation with light [IIDA15, KUB14, GUE15, TRY09, WAN14, YU15, ZAH15]. An early work on this topic is that reported by the Gütlich group (University of Mainz). However, in several reports, the light irradiation and the MS measurement are separated such as the experiment shown in Figure 3 [MKR09]. With increasing illumination time, the single absorption line shows significant line broadening and eventually splits into a doublet.

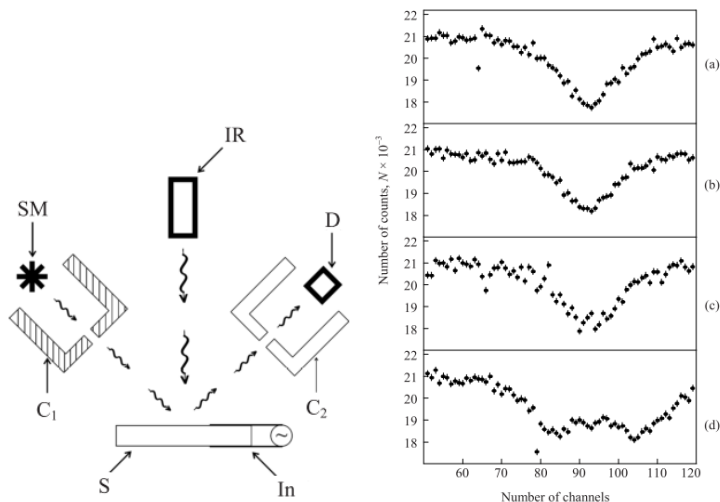


Figure 3: Left: Schematic drawing of the experimental setup for Mössbauer spectroscopy under irradiation: IR – infrared light source, SM – Mössbauer source (^{57}Co), D – porous detector (CsIAgSiO) for γ -radiation, S – probe ($\text{CdS}(0.2\% \text{ } ^{57}\text{Fe})$), C1 and C2 – apertures, In – electrical contact (made of In). Right: Mössbauer spectra of Cd a) un-irradiated, b)-d) irradiated with increasing time. (from [MKR09]).

Preliminary work: New Mössbauer setup and experiments at ISOLDE

1) New Mössbauer Spectroscopy setup

Prior to this application our group had successfully applied for a new Mössbauer spectroscopy setup as part of a BMBF funded collaboration (project number: 05K16SI1, represented at CERN by Dr. Juliana Schell as the solid-state physics coordinator). This Mössbauer spectroscopy setup is currently being built in lively exchange with the Mössbauer collaboration at ISOLDE and will be available for commissioning in 2018.

2) Mössbauer and TDPAC Studies of selected probes in hydrogenated thin films.

- Preliminary tests of hydrogen plasma treatment on our films were performed both with emission $^{57}\text{Mn}/^{57}\text{Fe}$ Mössbauer Spectroscopy (eMS) as well as $^{111\text{m}}\text{Cd}$ TDPAC studies on polycrystalline TiO_2 thin films (100 nm or 500 nm in thickness, with an average crystal size of around 25 nm), which were, depending on the synthesis temperature, belonging either to the rutile or anatase phase of TiO_2 , or a mixture of both. eMS is a powerful technique for gathering local information from ordered and structurally disordered regions of solids and is thus well suited for the atomic-scale characterisation of materials with high defect or impurities concentration, allowing to determine oxidation and valence states, crystal fields and site symmetry. The needed amount of probes does not exceed $10^{-3}\text{at}\%$ and therefore puts the least impact onto the physical properties of the host lattice under investigation. On the other hand, TDPAC, which also yields information about local crystal fields, gives a deep insight into interactions of $^{111\text{m}}\text{Cd}$ with point defects in the TiO_2 rutile lattice and the implanted amount is usually less than 10^{12} probe nuclei.

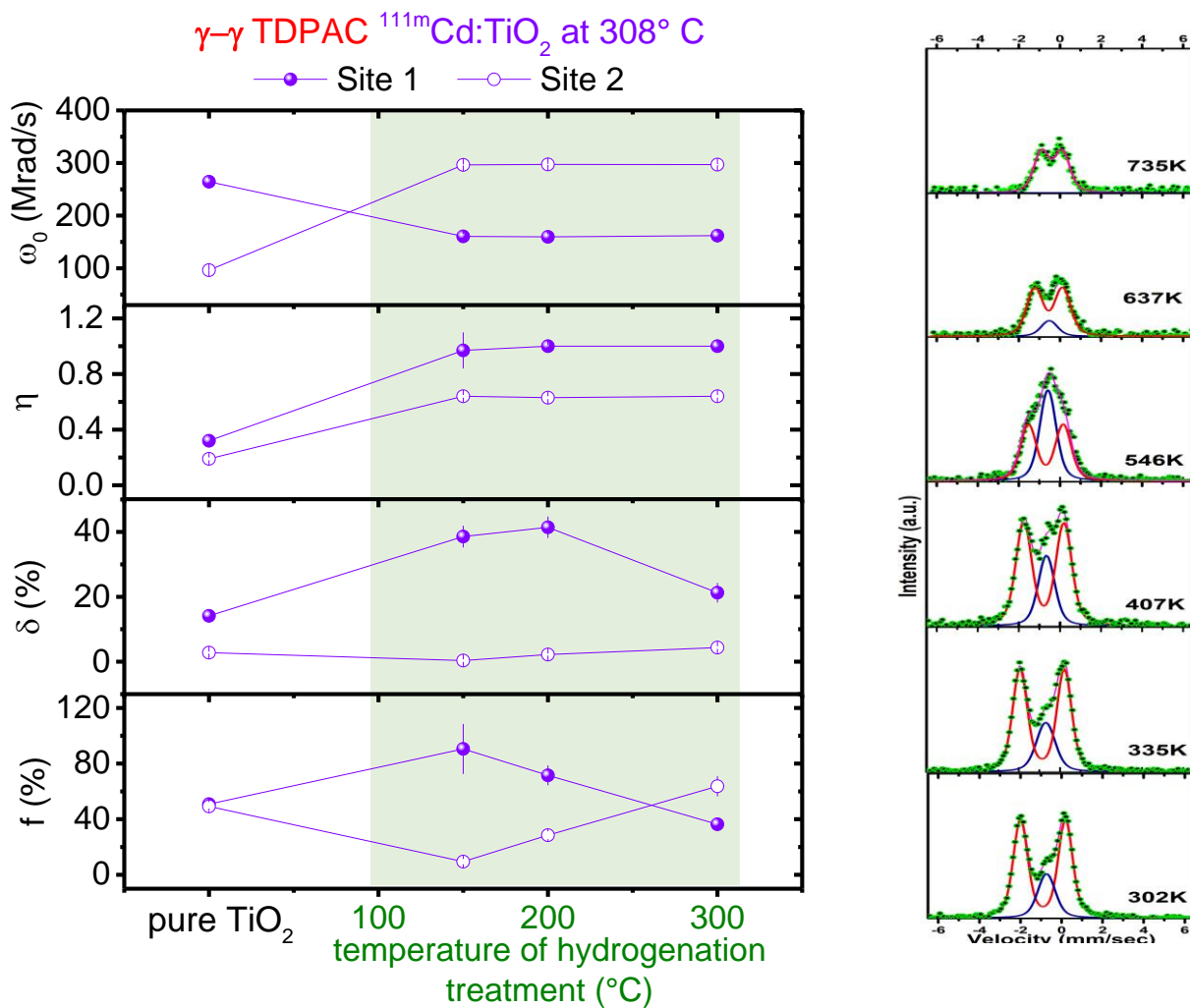


Figure 4 Left: Preliminary results of TDPAC measurements of ^{111m}Cd probes in $\text{TiO}_2:\text{H}$ thin films, measured at $T=500\text{K}$, for increasing hydrogenation treatment temperature. Right: Preliminary results of ^{57}Mn Mössbauer studies of $\text{TiO}_2:\text{H}$ films measured at various temperatures

In case of the $\text{TiO}_2:\text{H}$ anatase films, a temperature dependent eMS series using $^{57}\text{Mn}/^{57}\text{Fe}$ probe atoms was recorded, with an exemplary series for the $\text{TiO}_2:\text{H}$ films with hydrogen plasma treatment at RT shown in figure 4, on the right side. By choosing implantation energy around 30 keV, the near-surface region of the film (Fig. 5) can be probed. This is nicely correlated with the hydrogen doping depth of the sample, which normally does not exceed 15 nm, depending on the samples growth and hydrogen plasma treatment conditions. Overall, the spectra can be analysed in terms of a doublet due to Fe^{2+} , but around $T = 546\text{K}$, an apparent single line (SL) is additionally required to fit the data. The hyperfine parameters of the SL are neither consistent with pure Fe^{2+} or Fe^{3+} , but could be due to charge transfer (effective charge between 2+ and 3+ during the lifetime of the Mössbauer state) due to donor doping effects of H. This assignment is supported by XPS results on Ti ions in TiO_2 (not shown), and will be further investigated. On the other hand, a series of TDPAC studies were performed on $\text{TiO}_2:\text{H}$ rutile films for different plasma treatment temperatures with ^{111m}Cd probe atoms, with Cd known to enhance the photocatalytic activity when it is doped into

TiO₂ [AND09]. All measurements were performed at T=482 K. The results are shown in figure 4, on the left side (compare Ref. [SCH17]).

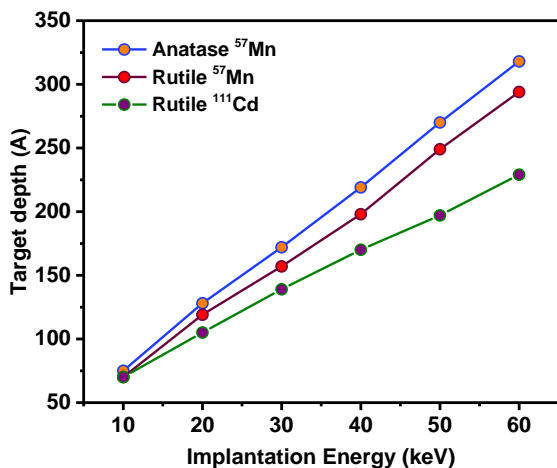


Fig 5: Computed mean implantation depths (using SRIM-2013, on SRIM see e.g. Ref. [ZIE10]) of selected ions ⁵⁷Mn and ¹¹¹Cd for various energies in Anatase and Rutile.

In summary, the main goals of the proposed project are:

- 1) Investigations, on an atomic scale, of defects formed in hydrogenated TiO₂ thin films and nano crystalline compounds as a function of hydrogen plasma treatment temperatures.
- 2) Test of the new online emission Mössbauer Spectroscopy setup that would allow eMS measurements to be made during light irradiation of samples.

Summary of requested shifts:

We are applying for the following beam time in 2018:

- 2 shifts for testing and commissioning of the new Mössbauer Spectroscopy setup
- 2 shifts of ⁵⁷Mn beam time
- 3 shifts of ¹¹¹mCd beam time

We are not applying for beam time beyond 2018 because of the long shutdown in 2019 and 2020.

In 2020, and application will be made for more beam time with an addendum to the present application, for experiments starting in 2021.

References:

- [AND09] L. Andronic, A. Enesca, C. Vladuta, A. Duta, "Photocatalytic activity of cadmium doped TiO₂ films for photocatalytic degradation of dyes", Chem Eng. Journal 152 (2009) 64-71. doi.org/10.1016/j.cej.2009.03.031
- [EU14] EU, Strategic Energy Technology (SET) Plan. 2014. ec.europa.eu/energy/en/topics/technology-and-innovation/strategic-energy-technology-plan
- [GAN16] A. S. Ganeshraja, K. Nomura, J. Wang, "119Sn Mössbauer studies on ferroelectric and photocatalytic Sn-TiO₂ nanocrystals", Hyperfine Interact. 237:139 (2016). doi.org/10.1007/s10751-016-1354-x

- [GUE15] P. Gütlich and Y. Garcia, "Spin Crossover Systems", in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier (2015) 1–4.
- [GUN14] H. P. Gunnlaugsson *et al.*, "Defect annealing in Mn/Fe implanted TiO₂ (rutile)", *J. Phys. D: Appl. Phys.* 47 (2014) 065501, doi.org/10.1088/0022-3727/47/6/065501
- [IIDA15] Y. Iida *et al.*, "Structural analysis and visible light-activated photocatalytic activity of iron-containing soda lime aluminosilicate glass," *J. Alloys Compd.* 645 (2015) 1–6. doi.org/10.1016/j.jallcom.2015.04.153
- [IVA14] S. Ivanov *et al.*, "Electrochemical lithiation of Si modified TiO₂ nanotube arrays, investigated in ionic liquid electrolyte" *J. Electroanal. Chem.* 731, (2014) 6–13. doi.org/10.1016/j.jelechem.2014.07.038
- [KUB14] S. Kubuki *et al.*, "Visible light activated catalytic effect of iron containing soda-lime silicate glass characterized by ⁵⁷Fe-Mössbauer spectroscopy", *J. Radioanal. Nucl. Chem.* 301, 1 (2014) 1–7. doi.org/10.1007/s10967-014-3109-y
- [MKR09] A. H. Mkrtchyan *et al.*, "Modification of Mössbauer Reflection Spectra of Group AII BVI Single Crystals with Fe 57 Nuclei under Influence of Infrared Radiation", *J. Contemp. Phys.* 44, 4 (2009) 194–196. doi.org/10.3103/S1068337209040082
- [NI07] M. Ni, M. K. H. Leung, D. Y. C. Leung, and K. Sumathy, "A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production", *Renew. Sustain. Energy Rev.* 11 (2007) 401–425. doi.org/10.1016/j.rser.2005.01.009
- [PJE15] D. Pjević *et al.*, "Properties of sputtered TiO₂ thin films as a function of deposition and annealing parameters" *Phys. B Condens. Matter* 463 (2015) 20–25. doi.org/10.1016/j.physb.2015.01.037
- [REN15] W. Ren *et al.*, "A Near Infrared Light Triggered Hydrogenated Black TiO₂ for Cancer Photothermal Therapy" *Adv. Healthc. Mater.* 4,10 (2015) 1526–1536. doi.org/10.1002/adhm.201500273
- [SCH17] J. Schell, D.C. Lupascu, J.G.M. Correia, A.W. Carbonari, M. Deicher, M.B. Barbosa, R.D. Mansano, K. Johnston, I.S. Ribeiro Jr., ISOLDE collaboration, "In and Cd as defect traps in titanium dioxide", *Hyperfine Interact.* 238:2 (2017) doi.org/10.1007/s10751-016-1373-7
- [SCH17B] J. Schell, P. Schaaf, D.C. Lupascu, "Perturbed angular correlations at ISOLDE: A 40 years young technique", *AIP Advances* 7 (2017) 105017. doi.org/10.1063/1.4994249
- [SUN17] G.A. Sundaram *et al.*, "¹¹⁹Sn Mössbauer and Ferromagnetic Studies on Hierarchical Tin- and Nitrogen-Codoped TiO₂ Microspheres with Efficient Photocatalytic Performance", *J. Phys. Chem.* 121 (2017) 6662–6673. doi.org/10.1021/acs.jpcc.6b12397
- [TRY09] B. Tryba, M. Piszcz, B. Grzmil, A. Pattek-janczyk, and A. W. Morawski, "Photodecomposition of dyes on Fe-C-TiO₂ photocatalysts under UV radiation supported by photo-Fenton process", *J. Hazard. Mater.* 162 (2009) 111–119. doi.org/10.1016/j.jhazmat.2008.05.057
- [WAN15] D. Wang, Y. Yan, P. Schaaf, and T. Sharp, "ZnO/porous-Si and TiO₂/porous-Si nanocomposite nanopillars", *J. Vac. Sci. Technol. B* 33, 1 (2015) 01A102. doi.org/10.1116/1.4891104
- [WAN16] Y. Wang *et al.*, "Structural and Magnetic Properties of ⁵⁷Fe-Doped TiO₂ and ⁵⁷Fe/Sn-Codoped TiO₂ Prepared by a Soft-Chemical Process", *Eur. J. Inorg. Chem.* (2016) 2131–2135. doi.org/10.1002/ejic.201501173
- [YA14A] Y. Yan, D. Wang, and P. Schaaf, "Fabrication of N-doped TiO₂ coatings on nanoporous Si nanopillar arrays through biomimetic layer by layer mineralization" *Dalton Trans.* 43 (2014) 8480–5. doi.org/10.1039/C3DT53409J
- [YA14B] Y. Yan *et al.*, "Slightly hydrogenated TiO₂ with enhanced photocatalytic performance," *J. Mater. Chem. A* 2 (2014) 12708. doi.org/10.1039/C4TA02192D
- [YAN13] Y. Yan *et al.*, "Understanding the fast lithium storage performance of hydrogenated TiO₂ nanoparticles", *J. Mater. Chem. A* 1 (2013) 14507. doi.org/10.1039/C3TA13491A
- [YAN15] Y. Yan, "Plasma-assisted synthesis of hydrogenated TiO₂," TU Ilmenau, 2015. d-nb.info/1082135402/34
- [ZAH15] K. Zaharieva *et al.*, "Preparation, characterization and application of nanosized copper ferrite photocatalysts for dye degradation under UV irradiation", *Mater. Chem. Phys.* 160 (2015) 271–278. doi.org/10.1016/j.matchemphys.2015.04.036
- [ZIE10] J. F. Ziegler, M. D. Ziegler, J. P. Biersack, "SRIM – The stopping and range of ions in matter (2010)", *Nucl. Instr. Meth. Phys. Res. B* 268,11–12 (2010) 1818–182. doi.org/10.1016/j.nimb.2010.02.091

Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
SSP-GLM chamber	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification
Mössbauer chamber (new and/or old existing chamber)	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
	<input checked="" type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input checked="" type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
Existing equipment in the SSP lab in building 508	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
	<input type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
[insert lines if needed]		

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

Hazards			
	Collection chamber and GLM beam line (SSP)	Mössbauer chamber at GLM beam line (SSP)	PAC lab (building 508)
Thermodynamic and fluidic			
Pressure			
Vacuum	typically 10 ⁻⁶ mbar	typically 10 ⁻⁶ mbar	typically 10 ⁻⁴ mbar (oven)
Temperature	RT	RT – 800K	RT – 800K
Heat transfer			
Thermal properties of materials			
Cryogenic fluid			
Electrical and electromagnetic			
Electricity		12 V, max. 5 A sample heating during measurements	
Static electricity			
Magnetic field	[
Batteries	<input type="checkbox"/>		
Capacitors	<input type="checkbox"/>		
Ionizing radiation			
Target material	TiO ₂	TiO ₂	

Beam particle type (e, p, ions, etc.)	ions	ions	
Beam intensity	10 ¹¹ ions/s	10 ¹¹ ions/s	
Beam energy	30 – 60 keV		
Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	<input type="checkbox"/>		
• Open source	<input type="checkbox"/>		
• Sealed source	<input type="checkbox"/> [ISO standard]		
• Isotope			
• Activity			
Use of activated material:			
• Description	<input type="checkbox"/> Collection in the chamber, removal from the chamber and transport to building 508	Measurement on-line with sample in the chamber	
• Dose rate on contact and in 10 cm distance	max. 10 µSv/h	max. 0.5 µSv/h	
• Isotope	^{111m} Cd	⁵⁷ Mn	
• Activity	max. 3-4 MBq per sample	max. 3-4 MBq per sample	
Non-ionizing radiation			
Laser		Illumination of the sample with laser light during Mössbauer measurements.	
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300MHz)			
Chemical			
Toxic			
Harmful			
CMR (carcinogens, mutagens and substances toxic to reproduction)			
Corrosive			
Irritant			
Flammable			
Oxidizing			
Explosiveness			
Asphyxiant			
Dangerous for the environment			
Mechanical			
Physical impact or mechanical energy (moving parts)			
Mechanical properties (Sharp, rough, slippery)			
Vibration			
Vehicles and Means of Transport			
Noise			
Frequency			
Intensity			
Physical			
Confined spaces			
High workplaces			
Access to high workplaces			

Obstructions in passageways			
Manual handling			
Poor ergonomics			

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*