

# SLS Symposium on

## Dynamics

**Tuesday, March 6, 2011**

**10:00 to 12:15, WBGB/019**

### **10:00 Time-Resolved X-ray Absorption Spectroscopy of Aqueous TiO<sub>2</sub> Nanoparticles**

*M. H. Rittmann-Frank, C.J. Milne, J. Rittmann, F.A. Lima, M. Reinhard, T. Rossi and M. Chergui*

### **10:30 In situ oxidation of shikimic acid particles under humid conditions**

*S. Steimer, E. Coz, G. Grzinic, A. Huisman, U. Krieger, M. Lampimäki, C. Marcolli, T. Peter, M. Ammann*

**11:00 Coffee**

### **11:15 Magnetisation Switching in Mesoscopic Structures studied with X-Ray Microscopy**

*Stephanie Stevenson, Christoforos Moutafis, Georg Heldt, Rajesh Chopdekar, Christoph Quitmann, Laura Heyderman, Joerg Raabe*

### **11:45 Magnetization dynamics of GdFeCo nanostructures revealed with PEEM**

*S. El Moussaoui, L. Le Guyader, M. Buzzi, L. J. Heyderman, F. Nolting, T. A. Ostler, J. Barker, R. F. L. Evans, R. Chantrell, A. Tsukamoto, A. Itoh, A. Kirilyuk, Th. Rasing, A. V. Kimel*

# Time-Resolved X-ray Absorption Spectroscopy of Aqueous TiO<sub>2</sub> Nanoparticles

**M. H. Rittmann-Frank, C.J. Milne, J. Rittmann, F.A. Lima, M. Reinhard, T. Rossi  
and M. Chergui**

*Ecole Polytechnique Fédérale de Lausanne, Laboratoire de Spectroscopie Ultrarapide, ISIC-FSB, CH-1015  
Lausanne, Switzerland*

*Hannelore.Rittmann-Frank@psi.ch*

TiO<sub>2</sub> nanoparticles have numerous applications including use as photocatalysts [1] and as semiconductor substrates in dye-sensitized solar cells (DSSC). [2] In order to understand the mechanism underlying such processes, we are interested in studying the fundamental photoinduced charge carrier dynamics in the colloidal semiconductor nanoparticles. Upon optical excitation of the titania nanoparticles, with energies larger than the bandgap (3.2 eV), an electron is promoted from the valence band into the conduction band and an electron-hole pair is created. The fast electron-hole recombination (<10 ps) competes with trapping processes of free charges on the surface and by lattice defects in the bulk. The trapped holes decay on timescales up to 250 ns, and the decay time for the trapped electrons ranges from 10's of ps out to the  $\mu$ s timescale. [3, 4] In this contribution, we present a study of the structural and electronic changes of TiO<sub>2</sub> nanoparticles after laser excitation by means of picosecond time-resolved X-ray absorption spectroscopy (XAS) at the Ti K-edge. The pre-edge peaks (<4.981 keV inset) are related to bound-bound transitions and contain information on the conduction band states of the semiconductor. The question relevant to our investigation is the correlation between electronic relaxation and the electronic and geometrical structural changes in the TiO<sub>2</sub> nanoparticles. On timescales beyond 50 ps the electron is likely in a trapped state, which are the relevant states for both photocatalysis and the electron transfer from nanoparticle to substrate in DSSCs. A preliminary analysis of our recent results measured at the microXAS and PHOENIX beamlines at the Swiss Light Source will be presented.

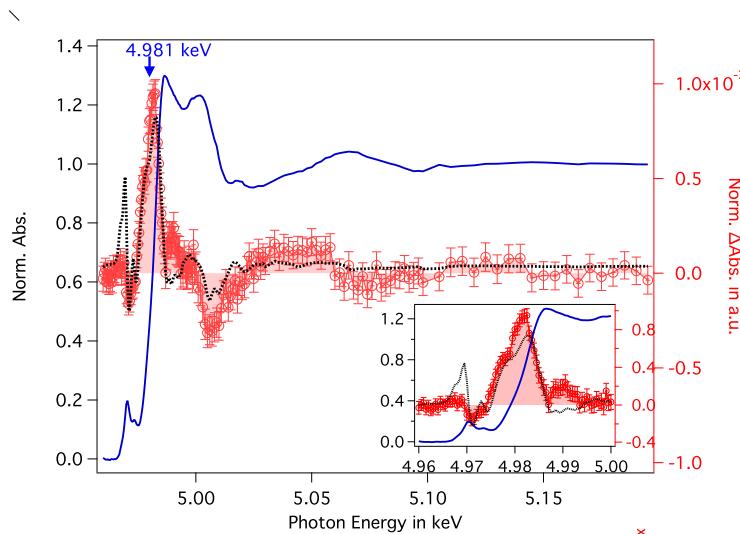


Fig. 1: The ground state Ti K -edge x-ray absorption spectrum (blue line) of TiO<sub>2</sub> nanoparticles together with the transient XAS difference spectrum (red circles) measured 100 ps after excitation. Inset shows zoom of pre-edge peaks.

## References

1. M. R. Hoffmann et. al. , Chem. Rev. 95 (1995) 69-96
2. N. Vlachopoulos et al., J. Am. Chem. Soc. 110 (1988) 1216-1220
3. G. Rothenberger, J. Moser, M. Gratzel, N. Serpone, D. K. Sharmaf , J. Am. Chem. Soc. 107 (1985) 8054-8059
4. H.A. Shkrob et al., J. Phys. Chem. B 108, (2004) 12497-12511

# In situ oxidation of shikimic acid particles under humid conditions

**S. Steimer<sup>1,2</sup>, E. Coz<sup>3</sup>, G. Grznic<sup>1,4</sup>, A. Huisman<sup>2</sup>, U. Krieger<sup>2</sup>, M. Lampimäki<sup>1</sup>, C. Marcolla<sup>2</sup>, T. Peter<sup>2</sup>, M. Ammann<sup>1</sup>**

<sup>1</sup> Laboratory of Radiochemistry and Environmental Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

<sup>2</sup> Institute for Atmospheric and Climate Science, ETH Zurich, 8092 Zürich, Switzerland

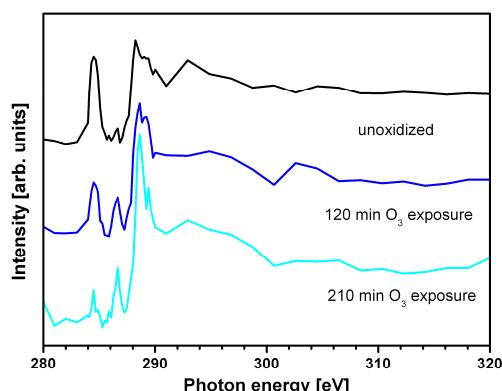
<sup>3</sup> Departamento de Medio Ambiente, CIEMAT, 28040 Madrid, Spain

<sup>4</sup> Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland

*sarah.steimer@psi.ch*

It has been shown that organic compounds can account for up to 90% of matter found in aerosols. Their chemical aging changes the physical and chemical properties and therefore the environmental impact of aerosols [1]. In the present study the aging of shikimic acid particles via reaction with ozone was investigated by scanning transmission X-ray microscopy (STXM) and near edge X-ray absorption fine structure spectroscopy (NEXAFS). An environmental micro reactor [2] enabled oxidizing the particles *in situ* under humid conditions.

The resulting spectra from the carbon edge show a clear change in spectral features upon exposure to ozone. The main differences between aged particles compared to fresh shikimic acid are a decrease in the double bond peak at 284.5 eV as well as an increase at 286.5 eV and a change in the region of the carboxyl K 1 s→π\* transition around 288.5 eV. These results show clearly that it is possible to monitor the oxidation of shikimic acid *in situ*. Considering the capability of the technique for spatial resolution, this opens possibilities for future studies of the progress of the reaction through the bulk and how it is influenced by changing experimental conditions. The microspectroscopy results will be combined with kinetic data from coated wall flow tube measurements to generate a more complete picture of the oxidation process.



**Figure 1:** Typical carbon K-edge spectra of shikimic acid particles before and after exposure to ozone, measured at 85% RH. The spectra are linear background subtracted and normalized to the mean intensity between 310 and 320 eV

## References

- [1] Y. Rudich et al., Chem. Rev., **103**, 5097 (2003).
- [2] T. Huthwelker et al., Rev. Sci. Instrum., **81**, 113706 (2010)

# Magnetisation Switching in Mesoscopic Structures studied with X-Ray Microscopy

**Stephanie Stevenson<sup>1</sup>, Christoforos Moutafis<sup>1</sup>, Georg Heldt<sup>2</sup>, Rajesh Chopdekar<sup>1,2</sup>, Christoph Quitmann<sup>1</sup>, Laura Heyderman<sup>2</sup>, Joerg Raabe<sup>1</sup>**

<sup>1</sup> Swiss Light Source, Paul Scherrer Institut, CH 5232 Villigen, Switzerland

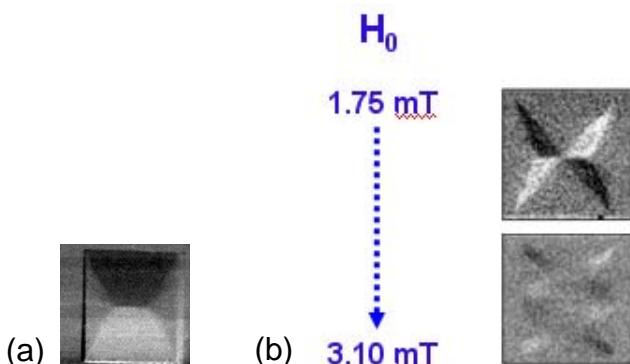
<sup>2</sup> Laboratory for Micro- and Nano-technology, Paul Scherrer Institut, CH 5232 Villigen

stephanie.stevenson@psi.ch

Magnetic domains have been used for data storage for decades. The performance of magnetic data storage is closely related to their internal magnetic structure and the physical properties of the materials used. Switching a magnetic structure involves dynamic and non-linear processes like precession and domain wall motion. We investigate microwave assisted switching processes of patterned magnetic elements, the study of which has impact on technological innovations and is of fundamental importance for the understanding of ultra-fast nonlinear magnetodynamics.

The main goals are to systematically study and subsequently optimise microwave assisted magnetisation switching in magnetic structures. Stroboscopic time-resolved imaging of resonant magnetic eigenmodes and the detection of switching events are carried out with energy and polarisation dependent Scanning Transmission X-ray Microscopy (STXM). These provide quantitative information about the magnetic state and its time evolution. The investigation is concentrated on Permalloy thin-film patterns with physical dimensions in the micron and deep sub-micron range.

In a first experimental step we are determining the eigenfrequencies as a function of the sample size and shape as well as the microwave power (CW) needed to induce switching. Recent results combine STXM data and simulations on magnetic structures with an induced in-plane uniaxial anisotropy. The domain configuration breaks up with an increase in applied CW power, returning to the ground state when the applied power is removed. Following on from these initial results, we will investigate controlled and optimised vortex core switching using adequately shaped RF-pulses.



- (a) XMCD image of the ground state of a  $6 \mu\text{m}$  magnetic structure with no excitation present. The vortex core is elongated due to the presence of an induced uniaxial anisotropy.
- (b) Differential dynamic images on the same structure under an excitation of 250 MHz with amplitude  $H_0$  indicate a breakup of the domain configuration at an excitation amplitude  $H_0 \sim 3.1 \text{ mT}$ .

# Magnetization dynamics of GdFeCo nanostructures revealed with PEEM

S. El Moussaoui, L. Le Guyader, M. Buzzi, L. J. Heyderman, F. Nolting

*Paul Scherrer Institut, 5232 Villigen, Switzerland*

T. A. Ostler, J. Barker, R. F. L. Evans, R. Chantrell

*Department of Physics, University of York, York YO10 5DD, United Kingdom*

A. Tsukamoto, A. Itoh

*Nihon University, CST, Chiba, Japan*

A. Kirilyuk, Th. Rasing, A. V. Kimel

*Radboud University Nijmegen, Institute for Molecules and Materials, Nijmegen, Netherlands*

The manipulation of spins is a very exciting topic from fundamental point of view as well as for practical applications. Combining experiments and simulation, we have been able to demonstrate that a fs-optical excitation is sufficient to trigger magnetization reversal in GdFeCo nanostructures on very short timescales. Employing a photoemission electron microscope (PEEM) at the SIM beamline, we have proved that we can manipulate the magnetization of nanostructures by using a heat pulse only. Performing time resolved X-ray magnetic circular dichroism (TR-XMCD) measurement we have observed that the magnetization reversal within the structures occurs on a timescale faster than 100 ps and evidenced that the reversal occurs against an external applied magnetic field. In our experiment the reversal happens only by heating the system on the time scale of the exchange interaction of the two sublattices and does not require any other external stimulus.

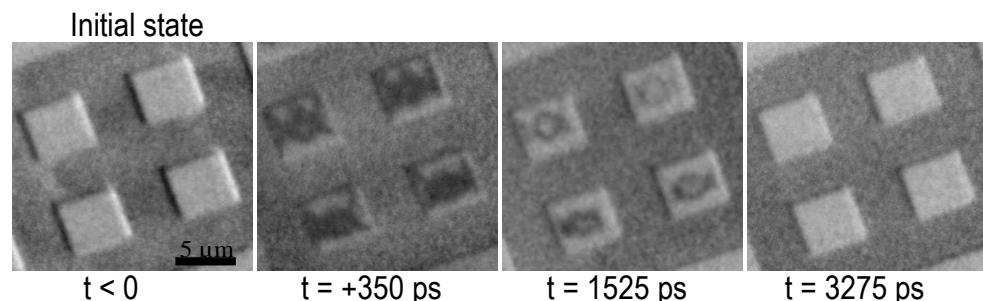


Figure 1: Sequence of TR XMCD images of GdFeCo taken at Fe L3 edge. The images show the magnetic configurations in 5  $\mu\text{m}$  squares imaged before the excitation with a linearly polarized laser pulse and at different delays after the laser excitation.

## Reference:

1. "Ultrafast heating as a sufficient stimulus for magnetization reversal"  
T. A. Ostler, J. Barker, R. F. L. Evans, R. Chantrell, U. Atxitia, O. Chubykalo-Fesenko, S. El Moussaoui, L. Le Guyader, E. Mengotti, L. J. Heyderman, F. Nolting, A. Tsukamoto, A. Itoh, D. Afanasiev, B. A. Ivanov, A. M. Kalashnikova, K. Vahaplar, J. Mentink, A. Kirilyuk, Th. Rasing and A. V. Kimel, *Nature Comm.* 3, 666 (2012).