C'NANO 2018
THE NANOSCIENCE MEETING
TOULON December, 11, 12 and 13
Palais des Congrès Neptune
In partnership with: Club nanoMétrologie

Thierry Epicier
DR CNRS
Materials, Engineering and Science (MATEIS), umr5510
Bat. Blaise Pascal, INSA de Lyon, 69621 Villeurbanne Cedex
Website: mateis.insa-lyon.fr/, http://www.clym.fr/fr/node/131
Email: thierry.epicier@insa-lyon.fr

CV/ biography (10 lines max.)
Thierry EPICIER is a Research Director within the CNRS in the field 'Chemistry of Materials, Nanomaterials and Processes". He works at the MATEIS laboratory (mateis.insa-lyon.fr/) at INSA de Lyon (National Institute for Applied Sciences). His activities deal with 'all-purposes' electron microscopy (SEM, TEM, FIB), with the aim of establishing correlation between structure, nano- and microstructures, and macroscopic and functional properties of (multi-)materials and nanomaterials, using imaging, High Resolution, tomography and spectroscopic analysis (EDX and EELS) and more recently Environmental and 3D operando TEM. He is currently the Deputy Director of the national 'TEM and Atom Probe' network METSA (www.metsa.fr, FR CNRS 3507). He was the General Physics Secretary of the French Society of Microscopies - SFμ (www.sfmu.fr) in 2010 and 2011 and chaired EMC2016 (www.emc2016.fr), the last European Microscopy Conference held in Lyon. As such, he has been a member of the EMS board since 2012.

Nanomaterials 'alive' under gas in the Environmental Transmission Electron Microscope (ETEM)

Abstract in the last decade, Environmental Transmission Electron Microscopy (ETEM) has become a new sharp blade of the 'TEM' Swiss Army knife for studying materials at the nanoscale in almost operando conditions. Spectacular technological improvements have been made for both dedicated ETEMs and E-cells [1], enabling today to follow a chemical reaction under gas and in temperature even down to the atomic level.
We will survey here several studies related mostly to nanocatalysts and conducted on the 80-300 kV Cs-corrected FEI-TITAN ETEM installed at CLYM in Lyon in 2013:
- The oxidation of soot by YSZ catalysts in the context of Diesel motors depollution [2]
- The interaction, and influence on atomic mobility of molecules (O_2, CO_2) with the surfaces of ceria (cerium dioxide CeO_2) nanocubes [3]
- In situ mechanical tests (i.e. nano-compression) of nanomaterials under various atmospheres [4]
Another challenging topic is the need for 3D information during the evolution of the object when exposed to reactive conditions. A high speed camera capable of acquisition rates at several hundreds frames per second (100 fps in 2K) allows fast 'tilting' tomography at the minute and even second level [5], which opens the way to quantitative 3D kinetics studies of nanomaterials such as nanocatalysts under operando conditions [6].

[1] "Controlled Atmosphere TEM", ed. T.W. Hansen, J.B. Wagner (Springer, New York), (2016), 332 p.
[2] A. Serve et al., *Appl. Catal. A*, **504** (2015), 74.
[3] M. Bugnet et al., *Nano Letters*, **17** 12 (2017), 7652.
[4] I. Issa et al., *Microsc. Microanal.*, **22** S5 (2016), 48.
[5] L. Roiban et al., *J. of Microscopy* **269**, 2 (2018), 117; H. Banjak et al., *Utramicroscopy* **189** (2018), 109; T. Epicier et al., *Microsc. Microanal.* **24** S1 (2018), 1814.
[6] This presentation is largely based on ongoing projects involving several colleagues at Univ. Lyon: L. Roiban, M. Bugnet, L. Joly-Pottuz, K. Masenelli-Varlot (MATEIS, INSA-Lyon); M. Aouine, F.C. Santos Aires, P. Vernoux, D. Lopez-Gonzalez (IRCELYON, UCBL); T. Grenier, H. Banjak, V. Maxim (CREATIS, INSA-Lyon). The support of ANR through the project 3DCLEAN n°15-CE09-0009-01 is gratefully acknowledged. Thanks are due to CLYM (www.clym.fr, a member of the METSA network - www.metsa.fr -) for the access to the ETEM funded through a CPER project 2007-13 associating the Rhône-Alpes region, the 'Great Lyon' and the CNRS.

Keywords: Nanomaterials, nanoparticles, heterogeneous catalysis, environnemental TEM, in situ, fast electron tomography,

11, 12 & 13 septembre
Session (Advanced characterisation)
Keywords: 'multiferroic; atom-scale STEM-EELS; structural defects; polarisation mechanism'

Cationic ordering in Ga2-xFexO : atomic scale characterisation of the polarisation walls

X. Devaux[1],. C. Bouillet [2], A. Demchenko[2] Ch. Lefevre[2], F. Roulland[2], D. Preziosi[2], S. Homkar[2], M. Vergnat [1]N. Viart[2]

1. Université de Lorraine, CNRS, Institut Jean Lamour (IJL), Nancy, France
2. Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), Strasbourg, France

The knowledge and control of the electric polarization in multiferroic thin films is currently the subject of extensive research efforts. This is the key toward a possible transformation into devices of the exciting phenomena such as conductance modification or polarity observed at ferroelectric domain walls. A considerable effort has been dedicated these last years to the exploration of the properties of ferroelectric domain walls, which show locally modified conductance or field effects.

The ferroelectric polarisation of the $Ga_xFe_{2-x}O_3$ structure can be easily observed along the c-axis by HR-STEM (Pna21, isomorphic to ε- Fe_2O_3). The thin layers that were studied here are composed of columnar nanocrystals with this axis mainly oriented along the growth direction. Extensive walls on which the polarization of the structure reverses can cross the nanocrystals perpendicularly to the c-axis. These walls separate areas whose polarization directions are oriented either face-to-face or tail-to-tail. HRSTEM images do not reveal clearly a breakdown of order in the inversion zone of the polarization, even if from HAADF imaging the polarisation inversion was identified in this structure on only one plane thick.
Spatially resolved STEM-EELS allowed visualizing the ionic ordering of the bulk. A different ionic structuration was identified in the seat of polarization inversions. Some walls also present steps at 45 °. The absence of gallium in these steps, suggests a high ionic mobility. Mechanisms of the polarization inversion of the structure during its stress by an electric field will be discussed.

11, 12 & 13 septembre
Session (Nano-materials, Advanced characterization)
Keywords: 'quantum dot, field emission, femto second laser'

Field Emission Spectroscopy of a nanodot at the Femtosecond Scale

Maxime DUCHET[1], Sorin PERISANU[1], Eric CONSTANT[1], Vincent LORIOT [1], Stephen PURCELL[1], Franck LEPINE[1], Anthony AYARI [1]

1. Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622, VILLEURBANNE, France

Field Electron Emission (FEE) is one of the earliest tool for surface science characterization and Field Ion Emission. Its counterpart, with opposite bias voltage, was the first process allowing the direct observation of individual atoms in 1955, more than 25 years before the scanning electron microscope. FEE is at the heart of modern characterization instruments in nanoscience such as scanning electron microscopy, transmission electron microscopy or far field scanning tunneling microscopy. Recently, several experiments on nano-tips irradiated by femtosecond laser have shown the great potentiality of FEE to get access to the ultra-fast electronic dynamics of nano-objects [1-3].

We recently developed a FEE experiments with an ultra-fast laser (14 fs pulse width and 80 MHz repetition rate). With this experimental set-up we have performed the first observation of the ultrafast electron dynamics of a 1 nm quantum dot by FEE of discrete energy levels with clear distinct features compared to metallic nano-tips.

[1] Yanagisawa H, Hafner C and Doná P. *Laser-induced field emission from a tungsten tip: Optical control of emission sites and the emission process*. Physical Review B, **81** (11): 115429 (2010).
[2] M Krüger, M Schenk, P Hommelhoff *Attosecond control of electrons emitted from a nanoscale metal tip* Nature **475** (7354), 78 (2011)
[3 G Herink, DR Solli, M Gulde, C Ropers *Field-driven photoemission from nanostructures quenches the quiver motion*- Nature 483 (7388), 190 (2012)

Congrès 2018, Toulon

11, 12 & 13 décembre
Session: Advanced characterization
Keywords: Nanoparticle, multimetallic, PDF analysis, DFT calculation

Ruthenium based multimetallic nanoparticles: how to probe the local structure?

Laura Ellezam[1,2], Capucine Sassoye[1], Caroline Mellot-Draznieks[2], Clément Sanchez[1]

1. Sorbonne Université, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, France
2. Collège de France, CNRS, Laboratoire de Chimie des Processus Biologiques, Paris, France

Ruthenia and ruthenium based nanomaterials are versatile and attractive candidates for various technological applications (electrochemical energy storage, catalysis, electrocatalysis…). As catalysts, they are well known for their high activity and selectivity. Oxide based materials are used as oxidation catalyst[1] while metallic ruthenium is mainly used for hydrogenation reaction.[2] In order to decrease the price of nanocatalysts and to increase the stability, we are introducing heteroatoms such as cobalt and are studying the consequences on the atomic structure and catalytic activity. Indeed, a rational understanding of the catalyst evolution[3] is crucial to further elaborate more efficient or new catalysts.

Nanoparticles are prepared using a one-step oxidative aqueous route[4].

To characterize the small (2nm) hydrous and doped nanoparticles, traditional laboratory analysis such as X-Ray Diffraction are not sufficient. We have therefore developed Pair Function Distribution analysis from a lab diffractometer. In parallel, DFT calculations are performed to propose structural models. For RuO_2, experimental PDF were successfully compared with DFT optimized models including water. Numerous cobalt insertion schemes are foreseen; For this reason, adapted Monte Carlo methods are used to propose several structural models, screened via DFT energy minimization.

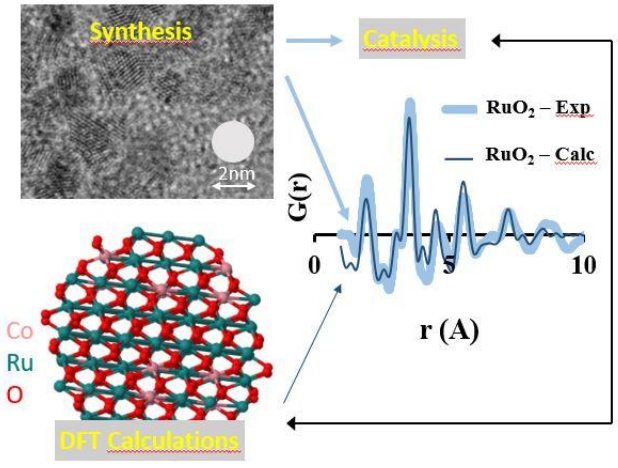

Figure 1: Loop between synthesis, PDF analysis and DFT calculations.

In conclusion, we have successfully built a methodology that consist of a loop between synthesis, experimental analysis (PDF) and calculation (DFT). (Figure 1)

1 Over, H. *Chem. Rev.* 112, 3356–3426, **2012**
2 Pakhare, D. et al. *Chem. Soc. Rev.* 18 (3), 293–301, **2015**
3 Over, H. et al. *Science* 287, 1474– 1476, **2000**
4 Sassoye, C. et al. *Green Chem*. 13(11), 3230, **2011**

11, 12 & 13 décembre
Nanochemistry, synthesis & assembly
Keywords: core-shell heterostructures, colloidal chemistry, magneto-elastic coupling, strain

Strain engineering of photo-induced phase transformations in Prussian blue analogue heterostructures

A. Adam[1], E. Larquet[1], O. Proux[2], D. Chernyshov[3], T. Gacoin[1] et I. Maurin[1]

1. *Ecole Polytechnique, CNRS, Université Paris-Saclay, Physique de la Matière Condensé, France*
2. *ESRF - The European Synchrotron, BM30B/FAME beamline, France.*
3. *ESRF - The European Synchrotron, BM1A beamline, France.*

Heterostructures based on Prussian blue analogues (PBA) combining photo- and magneto-striction have shown a large potential for the development of light-induced magnetization switching [1,2]. However, studies related to the microscopic parameters which control the transfer of the mechanical stresses across the interface and their propagation in the magnetic material are too scarce to efficiently improve the elastic coupling [2,3].

Here, this coupling strength is tentatively controlled by strain engineering in heteroepitaxial PBA core-shell heterostructures involving a same $Rb_{0.5}Co[Fe(CN)_6]_{0.8}.zH_2O$ photostrictive core and isostructural shells with a similar thickness and variable mismatch with the core lattice. The shell deformation and the quantification of the light-induced electron transfer at the origin of photo-striction are investigated by combined *in situ* and in real time synchrotron x-ray powder diffraction and x-ray absorption spectroscopy under illumination. These experiments show that rather large strains, up to +0.9%, are developed within the shell in response to the tensile stresses associated with the expansion of the core lattice. The shell behavior is complex, with contributions in dilatation, in compression or unchanged. We show that a tailored photo-response in terms of strain amplitude and kinetics requires a trade-off between the quality of the interface and the rigidity of the shell with respect to that of the core. A shell with a bulk modulus much smaller than that of the core will actually decrease its mechanical retroaction on the photo-switching properties of the core particles [4,5].

[1] Pajerowski et *al.*, Chem. Mater. **2011**, *23*, 3045.
[2] Risset *et al.*, J. Amer. Chem. Soc. **2014**, *136*, 15660.
[3] Dumont *et al.*, Inorg. Chem. **2011**, *50*, 4295.
[4] Presle *et al.*, J. Phys. Chem. C **2014**, *118*, 13186.
[5] Adam *et al.*, Nanoscale **2018** *10*, 16030

Congrès 2018, Toulon

11, 12 & 13 septembre
Session (advanced characterization)
Phase transition, TEM, in-situ, magnetism

Temperature dependent transition in MnAs : EMCD and electron holography in-situ studies

B.Warot-Fonrose[1], X. Fu[1], M. Eddrief[2,3], V. Etgens[2,3], R.Arras[1], V. Serin[1], C.Gatel[1]

1. CEMES, Université de Toulouse, CNRS, 29 rue Jeanne Marvig 31055 Toulouse Cedex 5
2. Sorbonne Universités, UPMC Univ. Paris 6, UMR 7588, INSP, 4 Place Jussieu, F-75005 Paris, France
3. CNRS, UMR 7588, Institut des Nanosciences de Paris, 4 Place Jussieu, F-75005 Paris, France

MnAs presents a remarkable magnetostructural phase transition from a ferromagnetic (FM) hexagonal α phase to a non-ferromagnetic orthorhombic β phase around 40°C with temperature rising. Most interestingly, the parameters of this first order transition are different in MnAs thin films grown on GaAs substrate compared to bulk MnAs. The thermal dilatation and crystalline transformation give rise to elastic strain that can be relaxed through the coexistence of α and β domains on GaAs. The temperature range where α and β domains coexist broadens and varies with the film thickness, orientation and deposition conditions.

Diffraction and EMCD experiments have been performed on MnAs thin films to follow the magnetostructural transition as a function of temperature and investigate the magnetic moments as a function of the crystallographic directions. The magnetic anisotropy of the EMCD has been measured and compared to DFT calculations.

MnAs thin film were also observed by in situ electron holography associated with temperature control to map the α and β domain coexistence. The magnetic induction of these alloys could thus be quantitatively mapped with a spatial resolution close to the nanometer during magnetic transitions. This approach revealed an inhomogeneous spatial distribution of the magnetic transition temperature along the growth axis. These results highlight the effects of the surface of the films but also of their interface with the substrate.

Beyond these results on the fundamental transition mechanisms, our work brings a new illustration of the interest of TEM experiments under sollicitation, here by the control of the temperature.