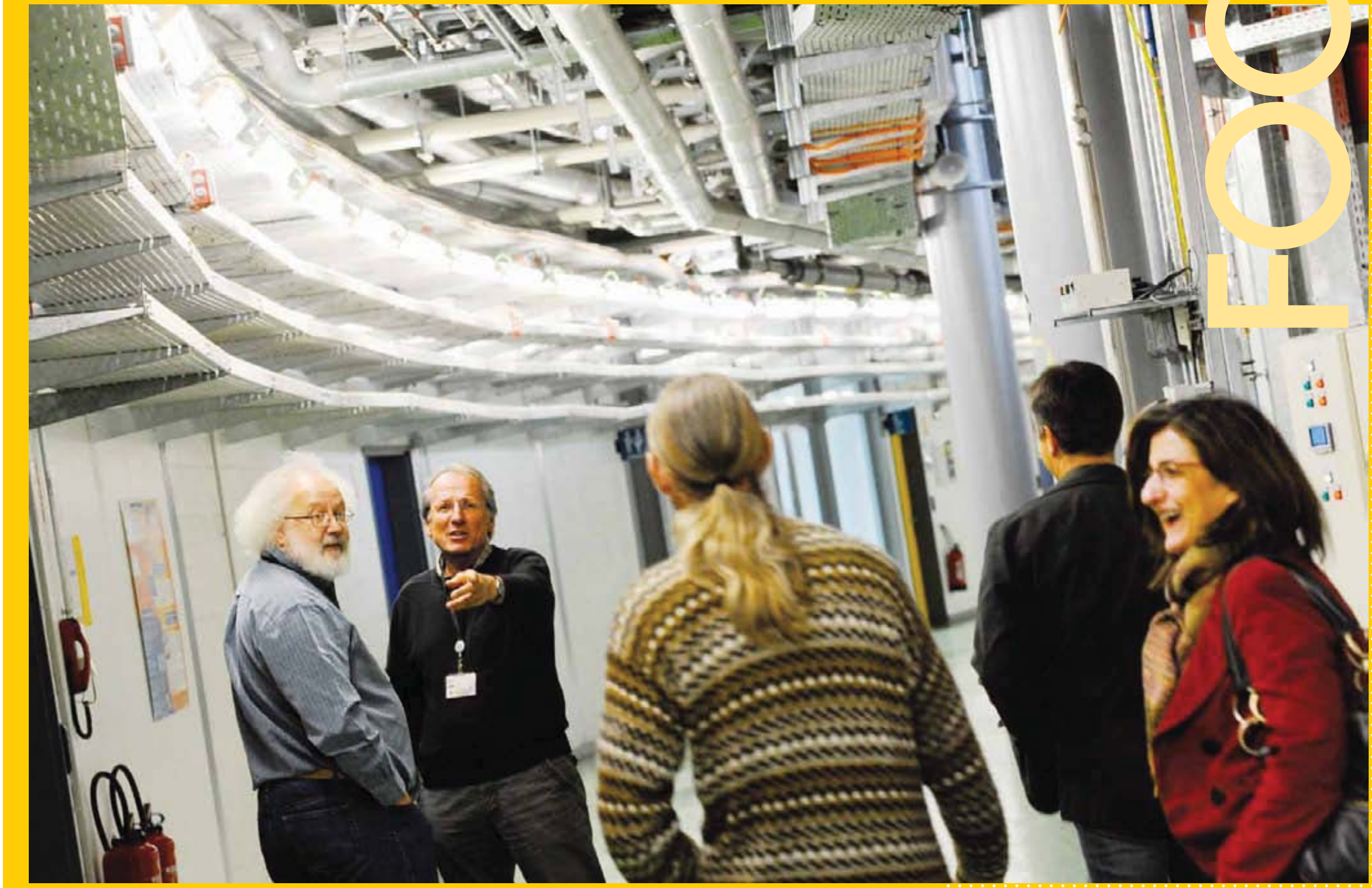
Research interdisciplinarity and results



Assessment of the four years since the light source and beamlines at SOLEIL have been operating now justifies all the choices made over the past ten years.

Research interdisciplinarity and results

Permanent interactions between the beamlines teams.

Beam stability, instrument quality and the expertise of the personnel who operate the facilities means that, in 2012, more than 3,000 users can now be accommodated annually on the beamlines, to achieve, under the best conditions, nearly 2000 projects and, since its opening to users in 2008, recorded nearly 500 publications in journals of high and very high impact factor (more than 2/3 of all the publications). Designed originally as specific beamlines in terms of method of analysis and scientific user communities, it is now clear that the borders between disciplines are fast disappearing and their interfaces are becoming more numerous. This wealth of science and innovation, which builds on the strengths of each discipline (chemistry, physics and biology, to name but three) continues to require the unique means of analysis and characterization of the SOLEIL beamlines, but in a new form: a single project now often requests several beamlines, able to analyze the same sample in a sequence of studies and applying defined methods. And that ideally includes the preparation of this sample on site at SOLEIL. This new approach to the use of SOLEIL can be illustrated by several examples.

Catalysis

Optimizing catalysis means mastering the reproducibility of the composition, preparation and structure of the catalyst material, in situ analysis of how it changes with use, and following the catalytic process itself under specific conditions of temperature and pressure. To do so, X-ray scattering to monitor the process of material nucleation and growth, X-ray absorption and fluorescence coupled to mass spectro-

SWING

Crystallization of quantum dots within a 3D biomimetic template

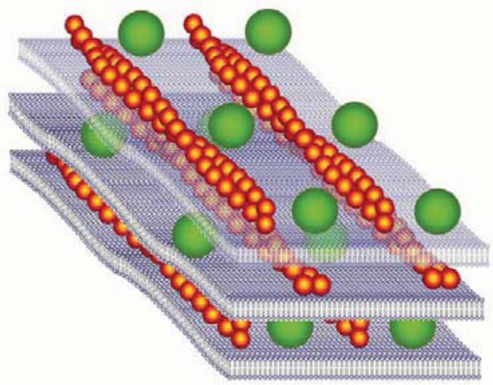


Figure 1 : schematic view of the structure. Strong electrostatic interactions between anionic microfilaments (red) and cationic lipids results in large undulations of the lipid bilayers (blue). Quantum Dots (green) are embedded between actin filaments as well as lipid membranes.

Generating new physical properties using the crystallization of nanoparticles is highly challenging. The design of such new materials with unexpected physical properties is thus the major motivation in the investigation of new strategies for controlling the crystallization of nanoparticles. In this context, biological molecules and molecular self-assemblies are promising templates to organize the spontaneous formation of structures of well-defined shapes and monodisperse characteristic sizes. Here is the report on the ability of a self-assembled three-dimensional crystal template of helical actin protein filaments and lipids bilayers to generate a hierarchical self-assembly of quantum dots (QDs; Figure 1). With this goal, functionalized quantum dots are incorporated during the dynamical self-assembly of this actin/lipid template through electrostatic interaction.
This slow mixing results in the formation of crystalline fibers. This process ensures the high quality of the crystal.
A very well-defined 3D crystal of QDs is then formed; its parameters (26.5 x 18.9 x 35.5 nm^3) are imposed by the membrane thickness, the diameter, and the pitch of the actin self-assembly. The inclusion of extraneous objects providing additional well-defined length scales is necessary to create 3D order, which is lost without actin.
The fluorescence properties of the 3D crystals of quantum dots demonstrate a direct effect of the nanostructuration of the quantum dots within the crystal.
Such a formation of 3D arrays of nanoparticles opens new route toward optical materials that are easily prepared by using self-assembling of vesicles, proteins, and hydrophilic nanoparticles in aqueous environment. This strategy could be extended to any kind of hydrophilic nanoparticles with various morphologies. Furthermore, the range of characteristic lengths can be extended by using other biological materials.

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Reference :
E. Henry et al. Nano Letters 11(12) (2011), 5443-5448

metry, photoemission and also tomography, are all complementary and necessary to answer the many complex questions aimed at optimizing, in terms of efficiency and cost, high value-added processes.

Life Sciences

Life sciences and health care, for which "Integrative Biology" and developments in regenerative and restorative medicine are major challenges to society, find at SOLEIL all methods of qualitative and quantitative analysis possible with third generation synchrotron radiation sources: X microscopy X, SAXS, IR & UV spectromicroscopies, biocristallography... Using these techniques, enriched by 3D imaging available soon on the Nanoscopium and ANATOMIX beamlines, SOLEIL addresses the need for multi-modal, multi-scale studies and characterization of Life, from the three-dimensional structure of macromolecules and their complexes to hierarchical tissue structures, via the cell and tissue distributions of chemical elements and therapeutic agents.

Material Sciences

The study of materials, often at the interface between physics and chemistry, is traditionally well established in synchrotron facilities, insofar as the characterization techniques (diffraction, scattering, absorption, fluorescence) are widely developed. SOLEIL largely meets this demand by providing many beamlines covering these techniques. Specific developments have led to more precise answers, often in collaboration with external support, for example by the increasing number of studies of materials under stress or in complex environments, or under extreme

To be continued on page 22...

PROXIMA 1

The 3D structure of surface proteins of the chikungunya virus has been elucidated

The chikungunya virus, spread by mosquitoes, causes infections the symptoms of which (severe joint pain), are similar to those of the dengue virus.

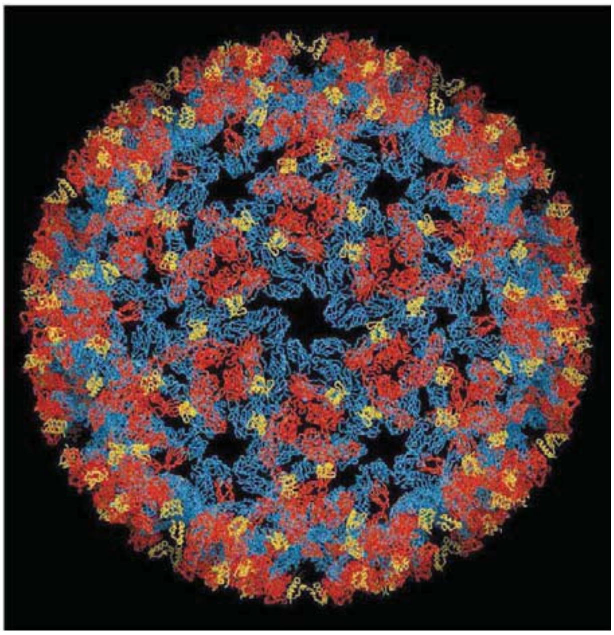

Figure 1: Surface of a particle of the chikungunya virus consisting of 240 E3/E2/E1 protein complexes (in blue/red/yellow, respectively)

The Pasteur Institute laboratory has been able to describe the atomic scale organization of proteins that form the outer layer of the virus and the structural changes related to the mechanisms of both invasion and production of new viruses.
Two protein complexes have been identified: p62/E1 and E3/E2/E1, the second from maturation of the first. The virus attaches itself first to the membrane of the target cell by means of E2. This membrane then surrounds the virus to enclose it in vesicles that transport it to successive cell compartments, endosomes, directing it towards the lysosome, responsible for dismantling it.
However, the pH of endosomes gradually becomes acidic, which activates E1. This protein will ensure the fusion of the viral and endosomal membranes, allowing the virus to release its RNA into the cell. And it is the cell machinery that will allow the virus to multiply after replication of the viral RNA.
Meanwhile, P62, insensitive to acidic pH, associates with E1 and allows the complex to migrate to the cell membrane. During this migration, p62 undergoes a maturation process, leading to the creation of E2 and E3.
The E3/E2/E1 complexes, thus formed, assemble to form new viral particles that bud from the surface of the infected cell and invade new cells.
Understanding these mechanisms shows that the stabilization of the E3/E2/E1 complex would prevent the virus from invading the cell.
The study also identified areas on E2 that recognize neutralizing antibodies, paving the way for new approaches to vaccines.
These studies make use of the low-resolution structure of protein complexes, obtained by cryo-electron microscopy, as well as the structure of the protein complex in its mature form, elucidated on the PROXIMA 1 beamline, in collaboration with the company Global Phasing Ltd (Cambridge).

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conditions of temperature and/or pressure, magnetic or electric fields. The use of coherent beams is developing to characterize, for example, the stress field at the interface, as well as high resolution and sensitivity tomography for 3D analysis. Special care is given towards ancient materials studies which require indeed a very specific sample preparation. Finally, time-dependent studies benefit from different modes of operation of the ring (1 bunch, 8 bunch, hybrid mode, low alpha) and there has been a particular growth in the development of femto-slicing to generate femtosecond pulses (see Rayon de SOLEIL 20, p11).

Knowledge of the fundamental properties of matter is a key issue in order to develop complex materials in the future or understand their behavior (control) on a large-scale or under external excitation. This often requires the development of complex experiments where a maximum of parameters are measured simultaneously. The decision by SOLEIL to develop «customized» beamlines (see page 6), where the technical choices on the source, optics, right up to detectors were pushed to the limit, has led to some original results, recognized in high-level publications.

PLEIADES

Imaging molecular potentials of ‘hidden’ states

A knowledge of electron-density distributions and potential energy surfaces of molecules is a key for predicting the physical properties and chemical reactivity of molecules.
The measurement of the energy of electrons, ejected by molecules as a result of their exposure to radiation, is one of the most commonly used methods to study different molecular states. Using traditional methods however, many electronic states cannot be accessed or they appear strongly overlapped with other states, which makes their isolation and characterization impossible.

The PLEIADES group, in collaboration with theoreticians from Japan and Sweden, has found a way to “pull-out” molecular states from the regions of overlap and reconstruct their potentials, otherwise inaccessible by other methods. Using resonant photoemission (RPE) spectroscopy, the molecular states of interest are reached not directly, as in traditional photo-electron spectroscopic methods, but indirectly via an intermediate state. This neutral, highly excited state is produced by absorption of a soft x-ray photon of a well-defined energy. Several femtoseconds after this absorption, the highly excited species thus produced relax by emitting a valence electron. However, in the intermediate state the molecule vibrates and has sufficient time to change its bond length. The probed part of the final state potential is different, therefore, from that probed by direct photo-electron spectroscopic methods, which can access only the so-called vertical transitions. In such transitions, the geometry is the same as in the ground state and no change of bond length takes place. By tuning the photon energy of the excitation radiation however, different vibrational levels of the intermediate state can be reached, which allows the width of the probed region in the final states to be controlled.
This technique is very demanding and requires high-brightness radiation sources owing to the dramatic decrease of the signal when tuning the excitation energy to higher vibrational levels of the intermediate state. Until now, such experiments can only be carried out on PLEIADES, but it will soon be possible to perform similar studies at the PETRA III synchrotron at DESY in Germany, and at MAX IV at Max-Lab in Sweden

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Reference : Miron, C. et al. Nature Physics 8(2)(2012) 135-138

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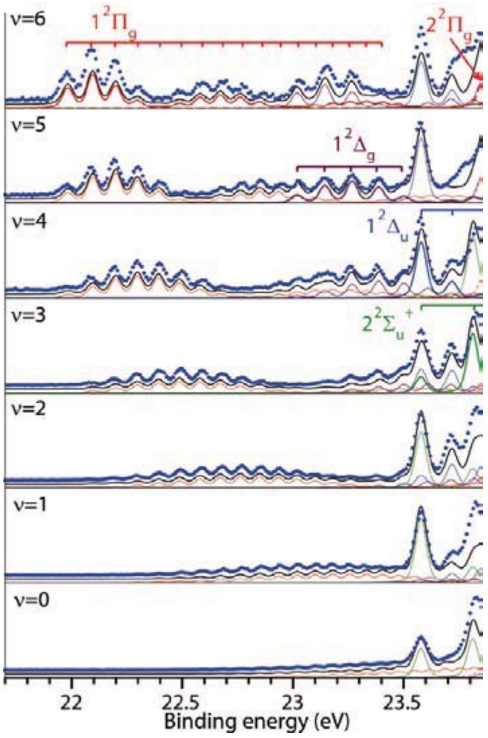

Figure 1: RPE spectra (dots) of nitrogen molecule recorded for a series ν = 0 – 6 of vibrational sub-states of the N1s→ π* core-excited state. Total and partial calculated cross sections are shown as continuous lines.

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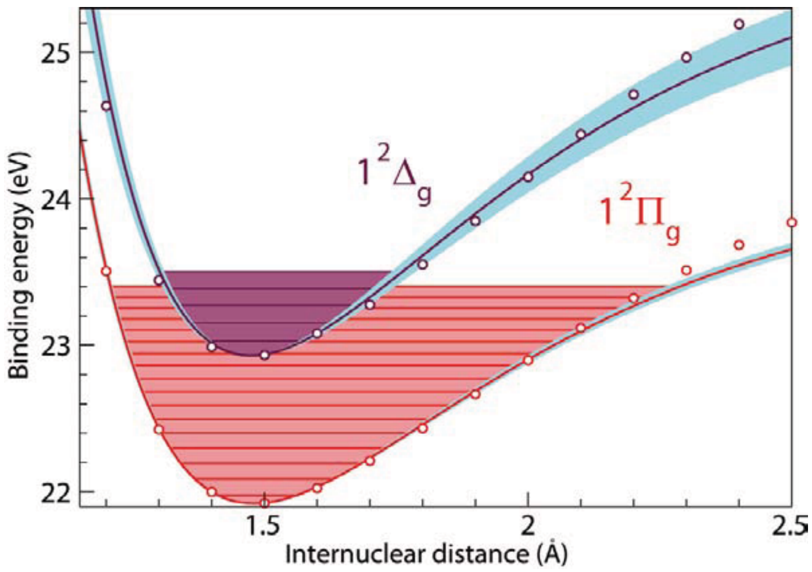

Figure 2: Comparison between the reconstructed molecular potentials based on ultrahigh resolution RPE data and ab initio calculated potentials (open circles). The error bars are shown as blue colored areas.

CRISTAL

Single bulk dislocations revealed by coherent x-rays in silicon

Dislocations are linear defects of crystals. They are involved in most of the physical properties of the crystals: mechanical properties of materials, electronic properties of semiconductors… Techniques like Scanning Tunneling Microscopy or Transmission Electron Microscopy provide atomic resolution images of dislocations, but the studied samples must not exceed few tens of nanometers in thickness; and the study of bulk dislocations remains a challenge. On the CRISTAL beamline, a combination of coherent x-ray diffraction and x-ray topography allowed to detect and get structural information about dislocations embedded a few micrometers beneath the sample surface. A Si(110) sample containing a few dislocations loops of about 100 mm in diameter was chosen as the model material to be studied. During a coherent x-ray diffraction experiment on a crystal, the intense beams reflected by the atomic planes of the crystal, known as Bragg reflections, are studied. If the sample is perfectly ordered throughout its illuminated volume, these reflections are single peaks. On the other hand, if the sample contains such defects as dislocations, the Bragg peaks split into two or more sub-peaks. In this study, the scientists first selected an isolated bulk dislocation by x topography. Then, they mapped it with a coherent beam of a few microns. Direct analysis of the intensity gives an image of the dislocation loop. Moreover, they observed a splitting of the Bragg reflection because of the dislocation, but the diffraction images provide further information about the core of the dislocation: a streak appears on the diffraction pattern meaning that the dislocation lines of the loop are dissociated into two parallel partial dislocation lines separated by a stacking fault, another classic defect in this material. Improvements in X-ray sources and optics will soon broaden the possible applications of this technique that also allows considering studies of phase defects in the bulk under various conditions such as magnetic or electrical field, high pressure, low temperatures…

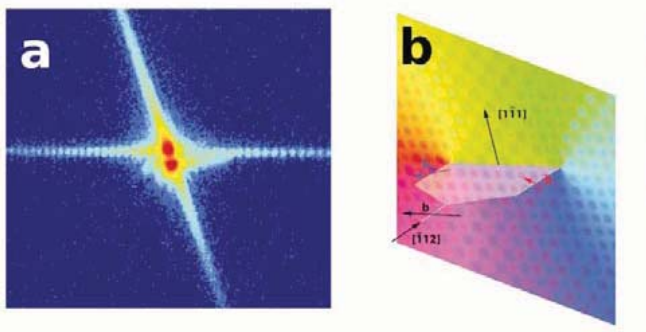

Figure 1 : (a) Coherent x-ray diffraction pattern measured at the 220 reflection when a dislocation line is illuminated. The Bragg reflection is split because of the phase shift introduced by the dislocation. A streak also appears due to the fact that the dislocation is dissociated into two parallel partial dislocations separated by a stacking fault.
(b) Schematic representation of a dissociated dislocation corresponding to the diffraction pattern shown in (a) and of the associated Burgers vectors, which gives the direction and amplitude of the atomic shift due to the dislocation.

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Reference : Jacques, V.L.R. et al. Physical Review Letters 106 (2011), 065502

SAMBA

An unprecedented structure of Re oxyde evidenced by *operando* XAS and Raman

Because of its high selectivity and the conciseness of the number of reactions required, the catalytic conversion of alcohols is an elegant way of yielding valuable products from biomass. Among possible reactions, the direct conversion of methanol (CH_3OH) to methylal ($CH_2(OCH_3)_2$) has drawn an increasing attention, both owing to its green chemistry implications and its relevancy as model reaction to probe bifunctional active sites. Practically, the gaseous methanol is contacted with the outmost surface of a divided catalyst where the reaction takes place. The present study is devoted to silica-supported oxorhenate catalysts, ReO_x/SiO_2. When prepared using the conventional impregnation technique, the material was less active and less selective than bulk ReO_3 or ReO_x/TiO_2.

The activity of supported oxorhenate catalysts were previously demonstrated as being highly correlated to the nature of support while the structure of the active phase was consistent with isolated ReO_4 moieties in tetrahedral coordination in all reported cases.

In order to solve the paradox, the scientists had previously proposed that differential hydration of the rhenium phase –possibly driven by the support- could influence the catalytic performance of the supported ReO_x materials rather than the support itself. The present work presents results obtained from a catalyst prepared using a one pot sol-gel based procedure.

At 240°C, the catalyst was 4 times more efficient than conventional Re/SiO_2 catalysts operating at the same temperature. Raman spectroscopy and rhenium L_{I-III} edge XAS gave insights on this peculiar activity. To this end, the spectra collection was performed simultaneously to the catalytic reaction using a dedicated spectroscopic cell making it possible to flow the reactants and control the temperature of the catalyst.

With Raman, two unusual stretching $\nu(ReO)$ modes are detected at 944 and 992 cm^{-1}, reflecting an original structure. Their intensity is visibly decreased under reacting

CASSIOPEE

Towards oxide-based multi-functional transistors

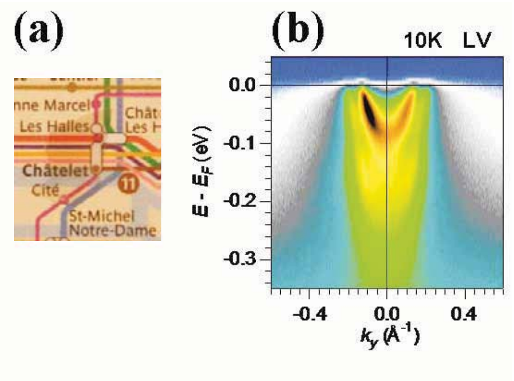

Figure 1 : (a) Photo of one of the insulating $SrTiO_3$ samples studied (with Paris metro map on the background). (b) Corresponding energy-momentum (E, k) density of electrons at 10K. The two free-electron parabolas are quantized energy levels due to the 2D confinement.

In the last 50 years, personal electronic devices have reshaped the ways we live, communicate and work. This revolution was made possible by the engineering of metal-oxide-semiconductor field effect transistors (MOSFETs), the two-dimensional electron gases (2DEGs) at the core of components for today's electronic devices. But the techniques used to create these integrated circuits will reach their 10 nm limit soon. In order to meet the growing demand of performances and miniaturization, alternatives are being explored. $SrTiO_3$, one of these alternatives, has been the subject of intense research. The interfaces between $SrTiO_3$ and other insulator oxides show two-dimensional metallic behaviour (even though the two constituents are insulators) and present interesting properties such as superconductivity, magneto-resistance, thermoelectricity... Furthermore, $SrTiO_3$ is non-toxic and its components are widely available in nature. However, the fabrication of these interfaces is difficult and costly to produce.

But an unexpected discovery has opened a new avenue for the generation and understanding of these 2DEGs. Originally studying the bulk electronic structure of $SrTiO_3$ for several dopings, an international team evidenced the presence of a highly metallic 2DEG, even in the case of bulk-insulating samples. By breaking a piece of $SrTiO_3$ under vacuum, the scientific team, led by researchers at Université Paris-Sud and CNRS, discovered that the bare surface of $SrTiO_3$ spontaneously develops this metallic 2DEG. The results were revealed by high-resolution angle-resolved photoemission measurements (Fig. 1b) carried out on CASSIOPEE beamline and in SRC (USA). Their results clearly evidence some bands crossing the Fermi energy E_F, i. e. being metallic. The metallic layer, two nanometers thick, is obtained through a simple and inexpensive process, potentially reproducible for other transition-metal oxides.

Such a discovery is a leap forward for the nascent field of oxide-based electronics. In the future, it could allow combining the intrinsic properties of a transition-metal oxide matrix with those of a 2DEG at its surface. For instance, one could imagine the realization of non-volatile memories by coupling a ferro-electric oxide with a 2D metal at its surface, or fabricating transparent circuits on the surface of photovoltaic cells or touch screens.

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Reference : A. F. Santander-Syro et al. Nature 469 (2011), 189-193

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conditions, suggesting that those frequencies feature a structural moiety which is implied in the reaction mechanism. To get to a better depiction of the new structures evidenced by Raman, operando XANES and EXAFS spectra were recorded on the SAMBA beamline using the Quick-EXAFS oscillating monochromator (cf Rayon de SOLEIL 18, p24).

The results are consistent with the existence of an unprecedented structure in which the ReO_4 tetrahedron interacts with water Re atoms by water molecules, as can be found in the bis-aquo adduct $Re_2O_7.2H_2O$.

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A. Yoboué et al. Chemical Communications 47(14) (2011) 4285–4287

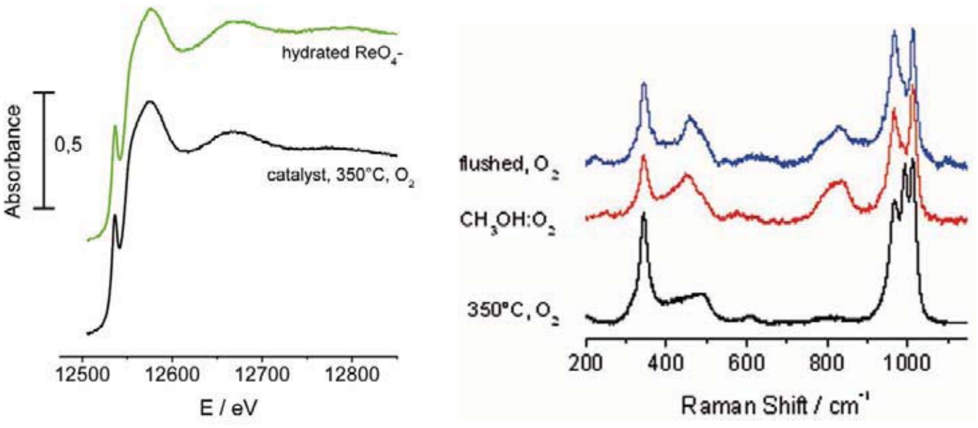

Figure 1: Left: compared XANES spectra recorded at the L_I Re edge of ReO_x/SiO_2 (O_2, 350°C) catalyst and aqueous ReO_4-. Right: Operando Raman spectra of the ReO_x/SiO_2 catalyst dehydrated at 350°C under O_2 (black), operating methanol oxidation at 240°C (red line) and subsequently flushed in helium and oxygen (blue line).