GILDA - GENERAL PURPOSE ITALIAN BEAMLINE FOR DIFFRACTION AND ABSORPTION - AT ESRF.

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1 Introduction

GILDA (General Purpose Italian BeamLine for Diffraction and Absorption), is the Italian CRG beamline, built to provide the Italian scientific community with an easy access to the European Synchrotron Radiation Facility to perform experiments with a high energy and brilliance X-ray photon beam. GILDA is operative since autumn 1994. Today GILDA is funded by the Italian public research Institutes: Consiglio Nazionale delle Ricerche (CNR) and Istituto Nazionale di Fisica Nucleare (INFN). Experimental stations for X-ray Absorption Spectroscopy, Anomalous X-ray Scattering and X-ray Diffraction (XRD) are present on the GILDA beamline.
The LNF group is involved in the technical maintenance and update of the beamline, with particular emphasis to the electronic and software controls of all the instrumentation.

2 Technical activity on the GILDA beamline during 2012

During 2012 the main implementations on the instrumentation were:

1. the installation and commissioning of a new hardware for controlling the vacuum operations in the EXAFS hutch. The new hardware is compliant with ESRF software; it consists in WAGO boxes linked to the control computer via ethernet and bearing modules for the remote control of pumping and venting of the experimental chambers, refill and pumping of the Ionization Chambers.

2. The installation of ICEPAPS hardware and SPEC software for the control of the stepping motors. Almost all motors are now controlled by the standard ESRF environment (SPEC) and can be used in automatic programs either under SPEC or Labview. The new system has permitted the development of automatic routines for the beamline alignment so at present the configuration change of mirrors (Pd/Pt/NoMirrors) can be realized in a couple of hours instead of a whole day in the past years.
   Now only the stepping motors of the monochromator are still controlled by the old VME-based system; this is mainly due to the considerable complexity of this device.

3. Implementation od the data acquisition under SPEC. The data acquisition programme permitted to access codes available at ESRF for data collection, like the XIA device server for the fluorescence detectors, and for data treatment that highly enlarged the experimental capabilities of GILDA. The possibility of collecting elemental maps on surfaces directly comes from this.

4. A new cryostat for the collection of XAS data on liquid samples down to 80K was built and installed on the beamline. The new cryostat cools the sample by a flux of cold gas: in this way no vacuum environment around the sample is needed. Working conditions have been determined: the new cryostat is compatible with both transmission and fluorescence data collection, can stand for about 20hrs of continuous operation before refilling and the samples are cooled down in about 30 minutes.

3 Beamtime use during 2012 and scientific outcomes

The beamline operation was deeply affected by the extremely reduced staff. It was possible to accept and perform only a limited number of easy experiments in XAS hutch.
After the long shutdown of ESRF, in order to restart with all the instruments correctly working, run 2012-I was totally dedicated to beamline commissioning. During the other runs 7 ESRF experiments have been carried out for a total number of 101 shifts delivered out of 124 requested by ESRF.

The remainder 372 shifts available were dedicated to beamline commissioning/test-with-expert-users.
During 2012, 32 paper were published in International journal with referee, the main topics being material science, catalysis, nanoparticles and cultural heritage. The following studies are to be mentioned:

1. *Bimetallic Gold −Palladium vapour derived catalysts: The role of structural features on their catalytic activity*
   A procedure to synthesize new AuPd bimetallic catalysts using Au and Pd vapours as reagents (metal vapour synthesis, MVS) is reported. The simultaneous co-condensation of Au and Pd vapours with acetone vapour affords AuPd/acetone-solvated metal atoms which have been used to deposit AuPd bimetallic nanoparticles on c-alumina and titanium oxide supports. Transmission electron microscopy (TEM) analysis determined the nanoparticles dimensions (d_m = 2.22.4 nm) and size distribution while the X-ray absorption spectroscopy (XAS) analysis showed the presence of small bimetallic AuPd nanoparticles with a large amount of AuPd bonds. The bimetallic co-condensed systems, tested in the selective oxidation of benzyl alcohol with molecular oxygen both in toluene solvent and in solvent-free conditions, showed higher catalytic activity and selectivity than the corresponding monometallic systems as well as of the analogous systems obtained by separate evaporation of the two metals.

2. *Silver Nanoparticles Stabilized with Thiols: A Close Look at the Local Chemistry and Chemical Structure*
   The local atomic structure and chemical nature of newly synthesized silver nanoparticles (AgNPs) functionalized with the organic thiol allylmercaptane (AM) have been probed combining synchrotron radiation-based techniques: Xray photoelectron spectroscopy (XPS) and X-ray absorption fine structure spectroscopy (XAFS). Complementary information about the chemical and electronic structure is obtained combining XAFS and XPS data. These results coherently suggest a core shell morphology of the NPs resulting in metallic Ag cores surrounded by Ag_2S-like phase. The external layer of AM molecules is grafted to the NPs surface through Ag-S chemical bonds. NP size and composition were found as a function of the chemical synthetic route (i.e., Ag/AM molar ratio). It was observed that by increasing the Ag/AM ratio, larger AgNPs were obtained. It was found that a higher Ag/AM molar ratio leads to an increasing of the Ag_2S layer thickness, while the external AM layer remains unvaried. TEM analysis showed well-separated and dispersed nanoparticles, and ED pattern allowed one to identify two different phases of single crystal corresponding to the presence of Ag face-center-cubic single-crystal symmetry, together with weak diffraction spots in agreement with Ag_2S cubic symmetry.

3. *Interaction of Cisplatin with Human Superoxide Dismutase*
   cis-Diamminedichloroplatinum (II) (cisplatin) is a chemotherapeutic drug that has been used to treat various types of cancer since the 1960s. In this paper, the interaction of cisplatin with human superoxide dismutase (hSOD1) has been investigated. Cys6 and Cys111 residues of hSOD1 have been claimed to be involved in the aggregation of demetalated hSOD1, which

may be associated with a neurodegenerative disease known as amyotrophic lateral sclerosis (ALS), the causes of which have yet to be understood. Here, the crystal structure of the cisplatin bound apo hSOD1 determined from XRD data (ID14-4 beamline) shows that cisplatin binds covalently the sulfur atom of Cys111. It also binds to Cu2-Zn2 and Zn2-Zn2 forms of hSOD1. The EXAFS data (beamline GILDA) of the cisplatin-bound apo hSOD1 indicates the same donor sets and equal coordination geometry for the Pt(II) ion in solution as in the crystal structure. Thus, also in solution cisplatin binds to a sulfur containing residue of hSOD1. Moreover, results of laboratory tests show that cisplatin inhibits aggregation of demetalated oxidized hSOD1 and it is further able to dissolve already formed hSOD1 aggregates in vitro and in cell, without affecting the hSOD1 enzymatic activity. From this work, cisplatin appears as a promising compound for the design of ALS disease treatments.

4. *Discoloration of the smalt pigment: experimental studies and ab-initio calculation*
Smalt is a deep blue pigment based on potassium silicate glass doped with Cobalt(II) ions. This revealed to be a fragile pigment as it tends to discolorate with time giving a grayish hue. In this contribution, fragments of a deteriorated painting (Il battesimo di Ges, Luca Signorelli, XV century) were analyzed via colorimetric, morphologic and structural analyses. A set of artificially aged smalt samples was produced and revealed to be identical, from a colorimetric point of view, to the original fragments. All specimens showed a depletion of K in the pigment grain when observed at the Scanning Electron Microscope. The K loss, presumably due to humidity, causes an acidification of the glass with consequences on the Co environment. X-ray Absorption Spectroscopy revealed a gradual shift from tetrahedrally coordinated Co in blue samples to a mix of tetrahedral and octahedral (30(providing a pink coloration of the matrix) provides a qualitative structural explanation for the discoloration. However, theoretical simulations of the optical absorption spectra of the various Co complexes by Time Dependent Density Functional Theory (TD-DFT) showed that octahedral complexes have a too low absorption to induce discoloration with only 30structures resulting from a partial protonation of the Co ligands provide at the same time high coordination and high optical absorption cross section and these are the correct complexes that cause the pigment deterioration.

5. *Development of a software package for EXAFS data analysis*
ESTRA and FitEXA are two programs for processing X-ray absorption spectroscopy data, extraction of extended X-ray absorption fine structure (EXAFS) signal, and EXAFS data analysis via least square refinement procedure (shell fitting). ESTRA and FitEXA propose useful options such as the analysis of the noise on the raw v(k) data and a high flexibility in the choice of the model distribution function: harmonic, anharmonic (cumulants) and hard sphere models. The minimization routines underneath the FitEXA code allow ample choice/control of the non-linear minimization procedure and check of the correlation among the parameters.

6. *Elemental mapping of surfaces*
By using a moderate microbeam (in our case 200μm*200 μm) it is now possible to collect at GILDA elemental maps of large surfaces (particularly useful in the case of natural stones or ceramic decorations) for which extreme microbeams (<5μm) are not suited. Tests have been carried out on ceramic samples; at each point illuminated by the beam a complete fluorescence spectrum is collected and successively images are retrieved by integrating suitable Region of Interest (ROI). This technique permits to characterize a sample before carrying out XAS spectra in selected points. It is also possible to realize maps of valence-state or local symmetry by using the change of shape of the XANES when an element changes its valence or the local symmetry (tetrahedral-octahedral). The same sample was investigated

by collecting the maps at particular energies, one far from the edge and the other on the top of the pre-edge peak of tetra-coordinated Fe^{3+} and taking the ratio. This succesfull experiment demonstrates how GILDA is effective in surface mapping on large surfaces and how additional information other then the simple elemental distribution can be obtained by using the tunable energy from the source.

4 2013 - GILDA Forseen Activity

During 2013 both the user facility operations and technical activities will be strongly influenced by the actual lack of personnel working on the beamline. For the user community the same criteria of 2012 will be adopted i.e. delivery of user mode only to ESRF experiments, operation with the sole Si(311) crystal, no experiments involving complex/dangerous sample environment and no diffraction experiment. In case of re-establishment of the correct staff level these procedures will be of course reviewed. The main foreseen activities for 2013 are:

1. Development of a new crystal mounting for an easy access to the high energy range (E>30 KeV) This will be realized by substituting the first Si(311) crystal with a couple of Si(311) and Si(755) in order to extend the energy interval to 30-90 keV. The intervention does not involve the delicate change of the second (curved) crystal as actually is. In this way a wide energy range (5.5-90 keV) will be available without needing further interventions inside the monochromator. The crystals have already been cut and will be mounted in the monochromator at the next machine startup.

2. Development of a data treatment software for reducing the effect of Bragg peaks present in the measurement performed the cold-chamber cryostat During exp. SC-3507 data at the Cu-K edge were affected by the presence of Bragg Peaks due to the frozen solution. Test will be carried out in order to develop a suitable data treatment procedure (fit of the raw fluorescence data, treatment of the dead time corrections) capable to reduce this effect.

5 Publications

1. C. Evangelisti *et al.*,"Bimetallic GoldPalladium vapour derived catalysts: The role of structural features on their catalytic activity", J. of Catalysis **286**, 224-236 (2012).

2. C. Batocchio *et al.*, "Silver Nanoparticles Stabilized with Thiols: A Close Look at the Local Chemistry and Chemical Structure", J. Phys. Chem C **116**, 19571 (2012).

3. C. Meneghini, F. Bardelli and S. Mobilio, "ESTRA-FitEXA: A software package for EXAFS data analysis", Nuclear Instrument and Methods B**285**, 153 (2012).

6 List of Conference Talks

1. A. Balerna ″EXAFS and XANES structural characterization of bimetallic AuPd vapor derived catalysts″, XAFS15: 15th International Conference for X-ray Absorption Fine Structure , Beijing (China), July 22-28, 2012.