Q1 # Characterization of catalytic materials with scanning photoelectron microscopy: Present and future

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ABSTRACT

Synchrotron-based scanning photoelectron microscopy has opened unique opportunities for exploiting processes occurring at surfaces and interfaces, which control the properties of functional materials where issues of complexity at microscopic length scales should be faced and understood. The present article aims at demonstrating the present capabilities of this microscopic method to explore the surface composition of micro- and nano-structured materials, focused on cases relevant to catalysis. We report and discuss some recent results about the chemical state of supported PtRh alloy microparticles under oxidation conditions and the changes in the status of a Co/polypyrrole electrocatalyst due to ageing in the course of the oxygen reduction reaction. Monitoring the lateral inhomogeneity in the chemical state at sub-micrometer length scales by combining chemical imaging and micro-spectroscopy has provided comprehension of events occurring at the catalyst surface, which determine the performance of the morphologically complex catalytic systems. Ongoing efforts for development and implementing of new set-ups that allow working closer to the realistic conditions of catalytic reactions are also outlined and briefly discussed.

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1. Introduction

Processes occurring at solid surfaces in contact with gas or liquid phase control the properties of many technologically relevant materials where issues of complexity at microscopic length scales, such as lateral inhomogeneity in the composition and/or morphology, should be faced and understood. In this respect surface science has made tremendous contributions shedding light on processes that lie at the heart of key technologies as catalysis, chemical sensors, bio-compatible implants, devices for energy conservation and production etc. Important frontiers in understanding interfacial phenomena have advanced thanks to the development of synchrotron-based photoelectron microscopes, which can perform chemical imaging and micro-spectroscopic analysis with lateral resolution better than 0.1 μm. The easiest approach for adding sub-micrometer lateral resolution to the chemical and surface sensitive X-ray photoelectron spectroscopy (XPS) is a set-up similar to the scanning electron microscopy, namely using an X-ray microprobe and scanning the specimen with respect to the microprobe. The performance of such instrument, called scanning photoelectron microscope (SPEM), was first demonstrated two decades ago [1] and their exploitation has become reality thanks to the tunable photon beams with very high brightness provided by the 3rd generation low emittance synchrotron radiation machines [2]. Since mid-90s of the last century SPEM has undergone tremendous improvements of imaging and micro-spectroscopic modes that have opened unique opportunities to examine nano-materials and events at solid surfaces and interfaces occurring at mesoscopic length scales [3,4,5,6,7]. SPEM methodology has also responded the increasing demand for visualization and characterization of individual free-standing nano-objects used in many modern devices, exploring in-situ lateral variations in their composition and properties as a function of shape, geometry, ambient, applied electric fields etc. [8,9,10]. Here, after short description of the working principles of SPEM we will report selected results for demonstrating the present capabilities for characterization of materials relevant to catalysis. Ongoing efforts for adapting SPEM to overcome the pressure gap limits and approach realistic ambient operation conditions will be outlined and briefly discussed as well.

2. SPEM instrument and experimental information

The microprobe in SPEM instruments is provided by photon focusing optics based on reflective (mirrors) or diffractive elements [11]. The most widely used are diffractive Fresnel lens optics called zone plates (ZP), which are circular diffraction gratings with a radially increasing line density. The ZP focuses the incident photon beam to a sub-micron spot onto the sample, allowing for probing variations in the photoelectron spectra, monitored by the hemispherical electron analyzer (HEA) in micro-spectroscopic method. In order to use only the first order

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diffraction and cut the undesired zero and high diffraction orders an order sorting aperture (OSA) is placed between the ZP and the specimen. It should be noted that the efficient use of the ZPs requires spatially coherent X-ray beams with reduced divergence, characteristics which can be provided only at the last generation synchrotron facilities. Compared to reflective optics, where diffuse light is a common problem, the ZP-OSA set-up provides a very clean micro-spot with dimensions determined only by the ZP outermost line width. However, it is fair to notify that although the ZP microprobe is reaching today a sub-10 nm diameter [11], realistic best lateral resolution for the SPEM set-up using soft X-rays is ~50 nm, mainly due to geometrical constraints, imposed by the ZP-sample focal distance [5,11]. A disadvantage of using ZP optics is their monochromaticity that makes it difficult to complement XPS with X-ray absorption spectroscopy since the focal distance changes with scanning the photon energy.

Fig. 1 shows a schematic drawing of the SPEM microscope at Elettra laboratory, operated in the soft X-ray range (350 to 1200 eV) using routinely microprobes providing lateral resolution 80–150 nm [4,5,12]. The main difference compared to classical XPS instruments is the fixed normal photon incidence geometry, imposed by the use of ZP focusing optics. This requires grazing acceptance angle of the hemispherical energy analyzer (HEA), usually ~45–50° with respect to the incident beam that is an optimal compromise considering that using soft X-rays the distance between the sample and OSA is rather short (5–15 mm depending on the photon energy and ZP parameters). Consequently, it is possible to vary the probing depth only by changing the photon energy or comparing the results and collecting electrons emitted from different core levels of the same element.

Apparently the micro-spectroscopy mode is identical to the classical XPS, i.e., electron energy distribution curves are measured from the irradiated micro-spot regions. In the imaging mode the HEA monitors the emitted photoelectrons with characteristic energies, usually tuned to selected elemental core levels, while scanning the sample across the X-ray microprobe. The potential and efficiency of the SPEM instruments have significantly been improved by implementation of multi-channel electron detectors, where each channel collects photoelectrons of specific kinetic energy within the selected energy window [7,13]. The number of simultaneously collected images is equal to the number of the channels, which makes possible with a single scan to obtain maps of different chemical states and of the background signal dominated by the surface topography. Reconstruction of the spectrum from selected parts of the images, so-called spectro-imaging, allows for discriminating differences in the local composition across the mapped sample region.

Indeed, SPEM cannot compete with the lateral resolution of 5–10 nm achievable by the X-ray photoelectron emission microscope (XPEEM) [5,6,14], but it has full versatility for probing samples with any shape and geometry. The best examples for SPEM potential in characterization of nano-structured materials are investigations of free-standing nanoscopic structures (nanotubes, nanowires and nanobelts) of different compositions [8,9,10,15]. This is illustrated by the top C1s image in
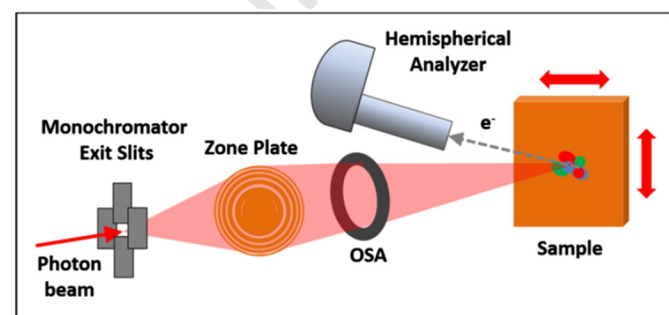

Fig. 1. Schematic sketch of the SPEM set-up, outlining the focusing system that consists of zone plate with a central stop and an order sorting aperture (OSA) that secure a pure first order diffraction microprobe.

Fig. 2(a), which shows vertically aligned carbon nanotubes (CNTs) of diameter ~70–80 nm, grown on a Si substrate. Such low-dense assembly of nanotubes allows for characterization of an individual nanotube even if its diameter is smaller than the photon microprobe size. The SPEM at Elettra can also use a special in-house designed setup to deposit confined micron sized patches of metals on the nanostructures. The two bottom images in Fig. 2(a), tuned to the C1s and Pd $3d_{5/2}$ core levels, show an example of an individual CNT (selected from the assembly), half covered with a Pd patch, where the confinement of the metal patch can be clearly seen. Fig. 2(b) shows the Pd $3d_{5/2}$ spectra taken in a micro-spot before and after exposure to oxidizing conditions, which illustrates the potential of SPEM to explore processes on nanostructures at sub-100 nm scales. The component with the lowest binding energy at 334.9 eV corresponds to metallic Pd, whereas the other two components are attributed to two different Pd oxidation states [16].

The model PtRh supported catalysts used for the studies reported in Section 3.1 were prepared by Pulsed Laser Deposition (PLD) technique using a PtRh (50:50 at.% alloy) target. The support was a 2–3 nm thick MgO film grown on a W(110) sample. The deposition parameters were chosen to produce a low particle density, approximately 1 particle/$10^4 * \mu m^2$ for particle sizes between 50 and 1000 nm, while the density of the smaller clusters (sizes <50 nm) was low enough to avoid the formation of a continuous film [17]. The preparation of the samples was performed in a small UHV chamber connected with the main SPEM chamber and they were transferred for characterization into the SPEM, avoiding the exposure to air.

Co/polypyrrole electrocatalyst samples, used for investigations of catalyst aging reported in Section 3.23.2, were synthesized electrochemically and annealed at high temperatures to improve their catalytic activity and durability. The procedure used for the fabrication and pyrolysis of these samples is described in Ref. [18]. The aging of pyrolyzed Co/PPy electrodes was carried out in a stagnant O_2-saturated 0.5 M H_2SO_4 electrolyte under quasi-steady-state conditions inside an electrochemical chamber connected to the SPEM, allowing operations at atmospheric pressures. Using an ultrahigh vacuum compatible transfer arm, the Co/PPy electrode was placed in contact with the electrolyte in a hanging-meniscus configuration and was the subject of electrochemical cycles, typical for catalyst aging conditions. After each ageing step the same area of the sample, transferred back to SPEM, was found and analyzed.

3. Results and discussion

3.1. Oxidation of supported PtRh microparticles

It has long been recognized that the catalyst undergoes chemical modifications under reaction conditions. For the case of reactions on metal catalysts involving oxygen different stoichiometric or transient oxide states have been considered as possible active catalyst states but all depend on the actual reaction conditions and also the surface structure of the catalyst plays an important role. Apparently, the chemical potentials of reactants are not compatible with classical surface science studies and in-situ investigations of transition metal single crystal and stepped surfaces using surface X-ray diffraction [19], ambient pressure XPS and ex-situ SPEM studies [20,21,22,23,24] have already provided very important information. SPEM results with Ru and Rh single crystal surfaces [21,25] have demonstrated the complexity even in the case of model catalysts, where the transient oxidation state is characterized with the development of laterally heterogeneity due to the coexistence of different metal oxidation states [21,26]. The catalytic properties and performance of metallic alloys are often superior than those of the respective single metallic catalysts [27,28] but this adds another factor to be considered — the segregation process. For the case of a PtRh alloy under investigation, used in chemical synthesis, exhaust gas converters and as an electrocatalyst [29], the Pt segregation trend can significantly be altered by kinetic limitations imposed by temperature