



Experiment title:
Element sensitive GIXF investigation of the Alkali cation insertion within a multilayer of conducting polyaniline.

Experiment number:
SC-2564

Beamline:
ID10B

Date of experiment:
from: 12 November 2008 to: 17 November 2008

Date of report:
12.02.2009
Received at ESRF:

Shifts:
17

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The experiment focused on an **element sensitive** investigation of the alkali cation insertion within a molecular layer of polyaniline in order to clarify the mechanism of modulation of its conductivity. Conductivity of poly-aniline (PANI) depends strongly on its doping level and redox state [1]: insulating emeraldine base form can be transformed into its conducting salt by doping, usually with hydrochloric acid. This form can be reversibly transformed to a non-conducting state e.g. by exposure to an alkali salt or to ammonia or electrochemically by applying to it a reducing or oxidizing potential. We characterized the doping mechanism both in the Langmuir monolayer on the water surface, and on multilayers deposited on Si for the structural characterization and on glass with Cr evaporated electrodes for the study of the doping/de doping mechanism.

Langmuir layers. In figure 1 (left) we report the GID profiles measured on PANI (M.W.>100kDa) at incident energy $\varepsilon=8063\text{eV}$ and impinging angle 75% of the critical angle, integrated in the Q_z range up to 0.2\AA^{-1} . The two curves correspond to PANI films in insulating form (pure water, circles) and conductive (0.1M HCl subphase, thick line). The two prominent peaks correspond to those recently found for truly metallic PANI solid layers [2,3] their distance in direct space corresponds to the size of a double phenyl ring and to the distance between coupled (piled) phenyl rings. We also measured X-ray reflectivity (right panel of the same figure) which is fitted by a 2 slabs model (see inset) with total thickness, 2.8nm, in agreement with our previous ellipsometric measurements. These results are important because they demonstrate that PANI polymer (at least with large enough molecular weight) forms homogeneous and well structured films at the air water interface even in its metallic, doped form [2].

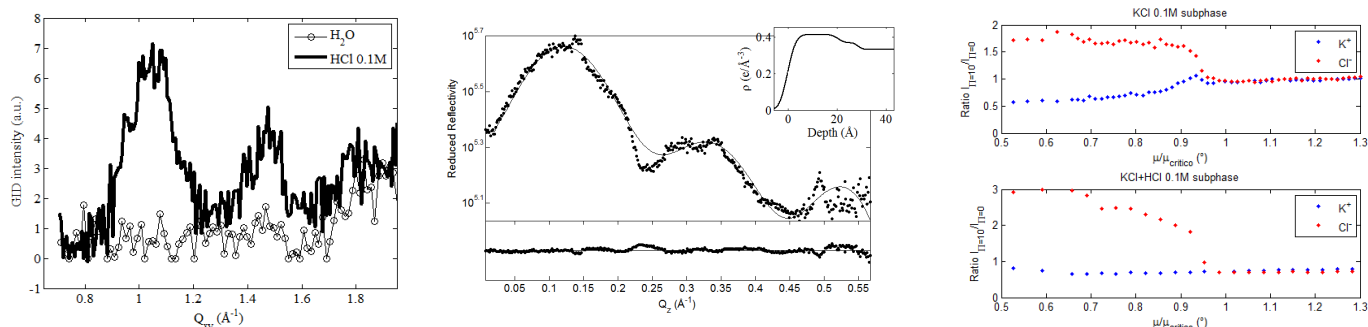


Figure 1, Left: GID patterns for insulating (on pure water) and conducting (on 0.1M HCl subphase) Langmuir films of PANI, measured at incident energy $\varepsilon=8063\text{eV}$ and impinging angle 75% of the critical angle, integrated in the Q_z range up to 0.2\AA^{-1} . **Center:** XRR reflectivity scaled by the Fresnel, with the best fit obtained with the 2 slab model sketched in the inset. **Right:** GIXF intensity from PANI film, normalized to the signal from subphase without film vs incidence angle, normalized to the critical angle.

In the right panel we report the GIXF spectra from Langmuir monolayers, normalized to the intensity measured on the same subphase without the film, as a function of the incidence angle normalized to the critical angle. Data were analysed in energy, and peaks were fitted in correspondence of the fluorescent emission of K, Cl and Ar (the later providing an internal consistency check) besides analysing the quasielastic (Compton) scattering used for data normalization. Upon HCl doping, a huge increase in the Cl signal is observed (data not shown), indicating that the doping process is not merely H^+ attachment to the film, but

also intercalation of excess H^+ whose excess electrostatic charge is balanced by the corresponding Cl^- . In the presence of KCl we note the expulsion of K^+ cations and the inclusion of Cl^- in the formed PANI film, which is reasonable taking into account the cationic nature of the PANI film (top right panel), while when both doping agents are present, a combination of the two effects is observed (bottom right panel).

PANI films deposited on solid substrate. For some unknown reason the XRR reflectivity of all the PANI films deposited on flat Si substrate invariably gave unstructured curves with no signature even of Kiessig fringes, albeit the morphology of the film, as checked by ellipsometry and SEM was optimal. Therefore we are not able to provide any structural evidence for the deposited films. We investigated the effects of exposing a PANI film, made of 48 monolayers, to HCl and NH_3 vapors. The sample was originally one of our device doped with KCl , so we expected to detect chlorine and potassium even before the exposition to the vapors. We recorded fluorescence as a function of the incidence angle below and above the critical angle, data were analysed in energy, and peaks were fitted in correspondence of the fluorescent emission of K , Cl , Cs and Ar (the later providing an internal consistency check) besides analysing the quasielastic (Compton) scattering used for data normalization. Different positions along the sample were recorded, with and without an applied voltage, so as to detect any change in the ion distribution. First we followed the process of doping of PANI by HCl vapors. In figure 2, left panel, we report the Cl intensity before and after exposition to HCl vapors, and subsequent dedoping by exposition to NH_3 . There is an obvious increase of Cl intensity, followed by its drop upon dedoping, while K and Ar intensities do not change (data not shown).

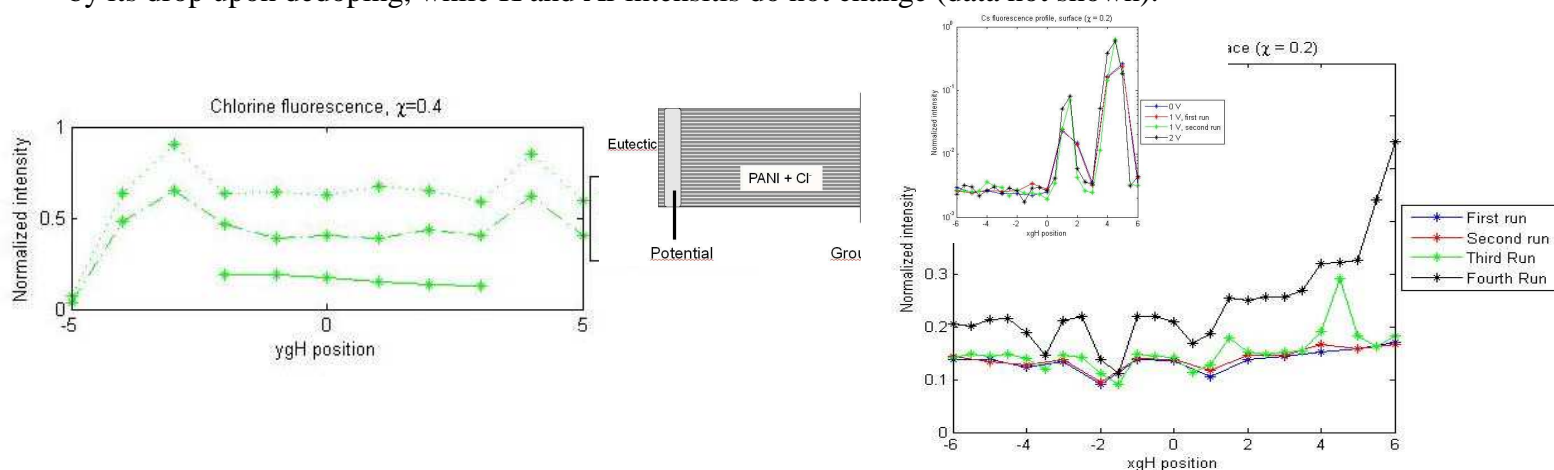


Figure 2, **left**: Distribution of Cl ions in pristine, in doped and in de-doped PANI film, **center**: a sketch of the device used, **right**: Cl^- and Cs^+ (inset) fluorescence intensity, as a function of the x-ray beam on the device.

Coming to the main objective of our proposal, we applied a voltage within the PANI film and observed the distribution of fluorescence from a 60 layer film of HCl -doped PANI. The electrical connections are shown in the mid panel of figure 2. We selected to work with Cs salt because of its high energy fluorescent emission. However a drawback of this choice was that Cs possesses intrinsically a lower ionic mobility.

In order to achieve some time resolution keeping the lateral space resolution, we measured fluorescence only at two values of the incidence angle, below and above the critical angle. We scanned the whole sample in 500 μm steps. We performed four runs: the first with no voltage applied, the second and the third applying a $-1 V$ bias, the fourth applying a $-2 V$ bias. Data intensities were corrected for the attenuator on the incoming beam, and normalized to Compton scattering, to account for geometrical effects due to the non ideal conformation of our sample. In the right main panel of fig.2 we report the fluorescence from Cl . Note that, when the bias reaches $-2 V$, there is a significant migration of Cl^- ions away from the negative electrode diffusing within the surface of PANI film (data taken with incidence angle below critical angle). On the same time the bulk of PANI film is not interested by the Cl^- migration (data not shown). Ar intensity was routinely checked. A more refined data analysis is in progress, however we anticipate that this is related to the mechanism controlling the conductivity of PANI films [4].

References

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