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Abstract
L-cysteine self-assembled monolayers (SAMs) have been deposited on gold from the liquid and vapour phase. Synchrotron based high resolution x-ray photoemission spectroscopy has been used to characterize the sulfur chemical states at the SAM/gold interface. Results obtained from pristine and x-ray irradiated samples, prepared with both as-received and purified L-cysteine, are reported. Pristine samples prepared with purified cysteine are characterized by an intense, largely dominant S 2p state at a binding energy around 162 eV ($2p_{3/2}$ level) assigned to thiolates. A second doublet around 161 eV develops during irradiation. By comparison with the literature, this doublet is assigned to atomic sulfur present either as impurity or generated by S–C bond scission. Comparative measurements performed, under similar experimental conditions, on pristine 3-mercaptopropionic acid [$HS(CH_2)_2COOH$] layers deposited from the liquid phase are also presented and discussed.

1. Introduction

Organic/inorganic interfaces are receiving increasing attention due to both fundamental and application interests [1]. A promising strategy for preparing bio-active surfaces exploits the self-assembly of molecules bearing sulphydryl moieties to transition metals. In this respect L-cysteine [$HSCH_2CH(NH_2)COOH$] (Cys) is an interesting molecule since, being an amino-acid, it can bind proteins to metallic surfaces [2–7]. Furthermore, because of its capability to coordinate ions, Cys has been exploited to prepare gold electrodes selective to copper(II) [8].

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The demand for stable and reproducible devices prompts the careful investigation of the SAM molecular structure and its dependence on the sample preparation protocol. Recently, Cys has been exploited to provide evidence for chiral discrimination in molecular interactions at surfaces [9]. Here we focus our attention on the Cys/gold interface by performing high-resolution x-ray photoelectron spectroscopy (HRXPS) measurements of the S 2p core level region of Cys SAMs deposited from the liquid and vapour phases onto gold films and single crystals, respectively. Comparative measurements performed on a similar system, 3-mercaptopropionic acid [$HS(CH_2)_2COOH$] (MPA) SAMs, deposited from the liquid phase are also reported.

2. Experimental details

L-cysteine (purity >99%, Sigma) was used both as-received and purified by re-crystallization in Milli-Q water. 3-mercaptopropionic acid (purity >99%, Fluka) and ethanol (purity 99.8%, Fluka) were used as-received.

SAMs prepared from solution were deposited onto gold films vacuum deposited onto mica, which exhibit a (111) texture (see [3] for details).

The gold films were flame annealed in a butane flame to a red glow, quenched in ethanol and immediately transferred into 1 mM Cys aqueous solution or 1 mM MPA ethanolic solution. The samples were kept in solution overnight at room temperature and after extraction they were thoroughly rinsed with the solvent and dried under a nitrogen stream.

Cys SAMs prepared from the vapour phase were deposited under UHV conditions onto a Au(110) single crystal by a two-stage differentially pumped source, described elsewhere [10]. Purified Cys powders were used.

HRXPS spectra have been measured at the ALOISA beamline of the ELETTRA Synchrotron (Trieste, Italy) [11]. Here we provide essential information relevant to this experiment. Samples prepared in liquid were inserted into the UHV experimental chamber by a fast entry-lock system. The Au(110) surface was prepared *in situ* by standard sputtering and annealing procedures. The cleanliness of the surface before deposition was checked by HRXPS which did not reveal any trace of common contaminants. The morphology of the surface was controlled by reflection high energy electron diffraction (RHEED) which showed a sharp (1×2) pattern indicating the well known surface reconstruction of Au(110). A p-polarized x-ray beam impinged on the sample surface at a fixed grazing angle of about 4.5° and the photoemission spectra were taken at normal emission by means of a hemispherical electron analyser with angular acceptance of 1°. Photoemission spectra were taken at several photon energies, in the range 270–700 eV. The experimental data are reported as a function of the binding energy (BE). The BE scale was calibrated with respect to the Au Fermi level and to the Au $4f_{7/2}$ peak at 83.97 eV.

The background due to inelastically scattered photoelectrons was calculated using the model proposed by Tougaard [12] and subtracted from raw data. Pseudo-Voigt (GL) functions, i.e. the weighted sum of a Gaussian and a Lorenzian function, have been fitted to the photoemission peaks. The S 2p doublet was fitted by a pair of GL peaks with the same full width at half-maximum (fwhm), the standard spin–orbit splitting of 1.2 eV, and a S $2p_{3/2}$/S $2p_{1/2}$ branching ratio of 2.

3. Results and discussion

The S 2p spectrum of a pristine Cys sample deposited from a solution of purified Cys is shown in figure 1(a). The best fit to the data was obtained with two doublets. Identifying the doublets
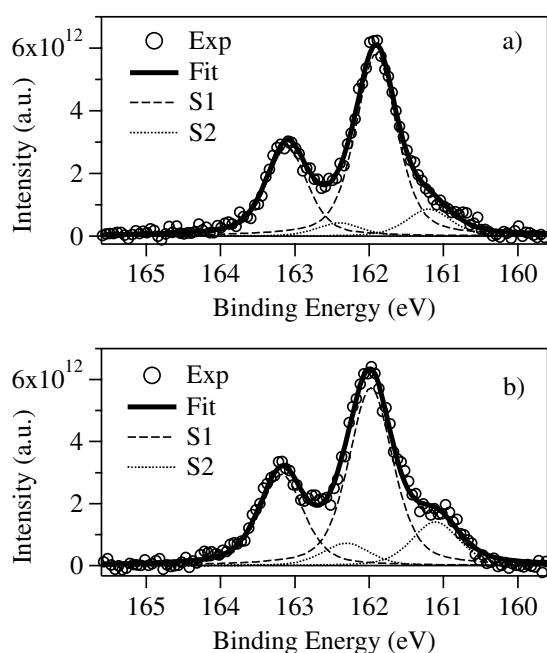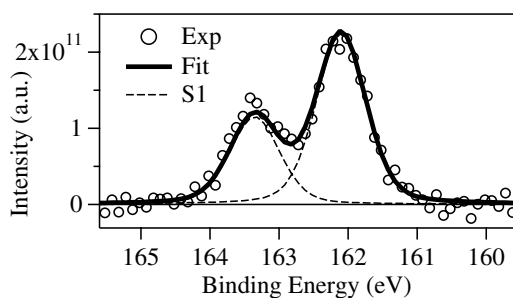
Figure 1. S 2p XPS spectra of Cys samples deposited from a solution of purified Cys: (a) pristine sample, (b) same sample after a 2 h irradiation with 270 eV photons at a photon flux of 7×10^{10} photon s^{-1}. Photon energy: 270 eV. Analyser pass energy: 10 eV.
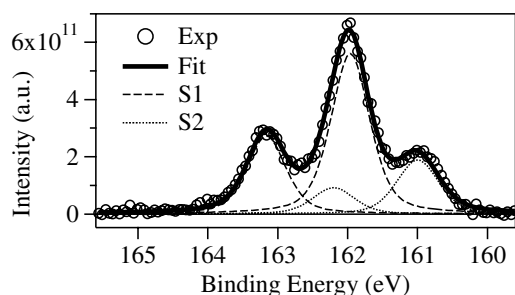
Figure 2. S 2p XPS spectrum of a Cys sample deposited from a solution prepared using as-received Cys. Photon energy: 390 eV. Analyser pass energy: 10 eV.

using the energy of their $2p_{3/2}$ component, the fit results in a main doublet (S1 species) at 161.9 eV BE. The fwhm (0.65 eV) is fully comparable with recent synchrotron based HRXPS experiments on related systems [13]. A low intensity doublet (S2 species) was found at 161.2 eV BE (fwhm = 0.7 eV).

Irradiation was found to cause the increase of the intensity of the S2 component relative to S1 together with the decrease of the carbon and nitrogen signals [10]. As an example, the S 2p spectrum of the sample of figure 1(a) after a 2 h irradiation with 270 eV photons is shown in figure 1(b). Similar effects were observed after moderate annealing (80–100 °C) of the samples (spectra not shown). The degree of purity of Cys powder influences significantly the S 2p signal. A typical S 2p spectrum of pristine Cys SAMs deposited from a solution of 'as received' Cys, is reported in figure 2 and presents a well developed S2 signal around 161 eV BE.

Figure 3. S 2p XPS spectrum of a ultra high vacuum deposited Cys sample. Photon energy: 690 eV. Analyser pass energy: 20 eV.

Finally, figure 3 shows the S 2p spectrum of a pristine SAM, deposited under ultra high vacuum conditions onto a Au(110) single crystal. Only the S1 state is observed.

As concerns the assignment of spectral features, the S1 state admits a plain interpretation. In facts, a sulfur chemical state with a BE of about 162 eV was already detected in early XPS experiments on Cys SAMs [14, 15] and is common to SAMs of organosulfur molecules on gold [13, 16–20]. It has been assigned to a thiolate species generated by the chemical reaction between thiol and gold. Accordingly our results confirm that Cys adsorbs on Au surfaces as a thiolate.

Comparison with previous high resolution experiments on other organosulfur SAMs [16, 19, 20] would suggest assigning the S2 state to atomic sulfur. This assignment finds definite support in a recent accurate photoemission characterization of the S/Au(111) interface [21].

Atomic sulfur could be present either as an impurity on pristine samples prepared with as-received Cys (figure 2 versus figure 1(a)) or as the result of C–S bond breaking in irradiated samples (figure 1(b) versus (a)).

The small S2 signal which is present in samples prepared with purified Cys (figure 1(a)) could be due either to residual impurities, still present after purification or formed during self-assembly. Contamination and alteration of the sample during the transfer into the UHV chamber should also be considered.

Furthermore, Ishida *et al*, in a study of annealing of organosulfur compounds [16], have pointed out a possible contribution of isolated sp-bonded molecules lying flat on the surface. In this respect we should consider that although flame annealed gold films exhibit large atomically flat (111) terraces [15], they are characterized by a higher density of defects (steps and grain boundaries) compared to single crystals. It could be speculated that cysteine molecules adsorbed at defects, i.e. with a different coordination compared to molecules adsorbed on flat terraces, could contribute to the S2 signal of figure 1(a).

We note that in previous works on Cys layers, a sulfur component at about 164 eV BE was identified [14, 15]. This species was observed in the present experiments only occasionally, with intensity much lower than the S1 signal, as a result of poor rinsing procedure. On the basis of these results we assign this state to weakly bound, second layer Cys molecules.

Control experiments were performed on MPA layers deposited on gold films from solution. MPA differs from Cys since the amino group is replaced by a hydrogen atom. The S 2p core level region of MPA is shown in figure 4. The analysis of the signal indicated the presence of two doublets. The best fit to the data was obtained with four GL functions with a fwhm of 0.7 eV. Similarly to pristine Cys samples, the main doublet (S1), at 162 eV, indicates the formation of thiolates. A second doublet (S3) was observed at higher binding energy. Note
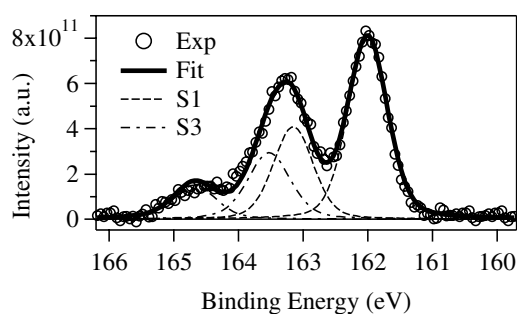
Figure 4. S 2p XPS spectrum of a pristine MPA sample. Photon energy: 390 eV. Analyser pass energy: 20 eV.

that the intensity of this state is rather low and the uncertainty on its position ($\sim$163.5 eV BE) is large. Interestingly there was no evidence of the S2 state around 161 eV BE. This finding seems to rule out two of the hypothesis about the origin of the S2 state of figure 1(a) mentioned above, e.g. the role of substrate defects and contamination effects during transfer.

Concerning the S3 state of MPA, angle resolved XPS measurements indicate that the S3/S1 intensity ratio increases at grazing photoemission angles (data not shown). This observation indicates that the S3 species lies above the S1 species and suggests the assignment of S3 to an 'unbound sulfur' state. In this respect, we note that in a study of a related system such as 4-mercaptohydrocynnamic films, a sulfur component at 163.7 eV BE was attributed to second layer molecules hydrogen-bonded to first layer molecules via carboxy groups [22]. The assignment of a S 2p signal around 163.6 eV to unbound molecules was also reported for poorly rinsed long chain alkanethiol SAMs [23].

On the other hand a S 2p component around 163.2–163.4 eV was found on long chain alkanethiol SAMs damaged by x-ray radiation. This sulfur species was attributed either to disulfide formation [24, 25] or, more recently, to the incorporation of sulphide entities into the alkylic chains [26].

In our measurements the S3 signal intensity was not significantly affected by irradiation (data not shown) which instead caused a major change on the low BE side, with the rise of the atomic sulfur state, similar to the results obtained on Cys. Therefore our results could suggest the presence of unbound molecules and/or disulfide moieties in pristine MPA samples.

In conclusion HR XPS experiments allowed us to fully characterize the S 2p states at the Cys/gold interface either prepared from solution or UHV deposited, disentangling the thiolate contribution from the spurious atomic sulfur contribution related to impurities and irradiation damage.

We note that in spite of the relative similarity of the molecular structure, the HR XPS spectra of Cys and MPA SAMs present significant differences, likely related to the SAM molecular packing and structure. These differences deserve further investigation extended to C 1s, O 1s and N 1s core level regions in order to better understand how the subtle interplay of the substrate/molecule and molecule/molecule interaction can affect the layer structure. In particular work is in progress towards the electronic and structural characterization of vacuum deposited Cys films ranging from submonolayer to multilayer coverage.

Acknowledgments

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