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- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Electrochemical Intercalation of Metals Into Organic Thin Films	**Experiment number**: CH1280
Beamline: ID26	**Date of experiment**: From: 12/6/02 to: 18/6/02	**Date of report**: 23/2/03 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Dr. Thomas Neisius	
Names and affiliations of applicants (* indicates experimentalists): Jonathan Lee* (University of Cambridge, Department of Chemistry) Dr. Trevor Rayment* (University of Cambridge, Department of Chemistry) Dr. Antje Vollmer* (University of Cambridge, Department of Chemistry) Rachel O'Malley* (University of Cambridge, Department of Chemistry)		

Report:

Introduction

The primary objective of experiment CH-1280 was to determine the local structure of Cu ions deposited electrochemically onto an Au(111) electrode covered with organic alkane thiols. To fully characterise this system, the experiment fell into two distinct sections.

Initially, X-ray Absorption Spectroscopy (XAS) measurements were undertaken to probe the local environment of a single monolayer of Cu atoms electrodeposited, via underpotential deposition (UPD), onto a bare Au(111) electrode surface. Since this system has been extensively studied by a variety of techniques it was investigated, in part, to act as a reference against which additional experiments could be compared. Further, we believe that although XAS has previously been employed to examine the change in structure of the monolayer, with increasingly reducing potential, this is the first study to include fitting the Extended X-ray Absorption Fine Structure (EXAFS) with computer generated 3D models (EXCURV98).

Most of the time was used to elucidate the structure of a Cu adlayer intercalated into an interface comprising the electrode and a supported monolayer of organic material. The properties of the Au(111) surface can be modified by development of a well-ordered self-assembled monolayer (SAM) of alkanethiol molecules. Deposition of a monolayer of metal atoms onto the electrode from electrolyte solution may be achieved *through* the SAM to provide an interface of the form Au(111)/metal monolayer/SAM (figure 1), which shows increased resistance to oxidation of the metal adlayer and to electrochemical desorption of the SAM.

Butanethiol was chosen to form the organic overlayer (BTSAM) and modification of the Cu environment was monitored as a function of applied potential. The bare and surface modified systems were investigated with the plane polarisation of the incident X-ray beam perpendicular to the surface plane of the Au electrode.

Experimental

Electrodeposition of the metal adlayers was achieved in a purpose built electrochemical cell that permitted X-rays to reach the electrode surface and fluorescent photons to leave the interface through a thin polymer (mylar) ‘window’. Monolayer concentrations for both systems are within the range ca. $4x10^{14}$ – $1.5x10^{15}$ atoms cm^{-2} and were established via deposition with the mylar film inflated with excess electrolyte. During XAS measurements, solution contributions to the fluorescence signal were minimised by using 0.1mM Cu^{2+} solutions and deflating the polymer window such that only 5 microns of the electrolyte was held above the electrode surface. We estimate the solution contributes less than 5% to the total signal.

Figure 1: The SAM/adlayer/Au interface

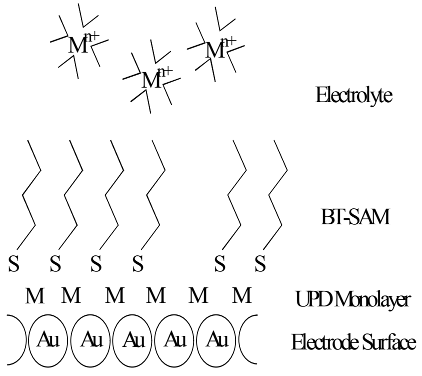


Figure 2: CV of Cu deposition on a bare Au(111) surface (XAS Cell)

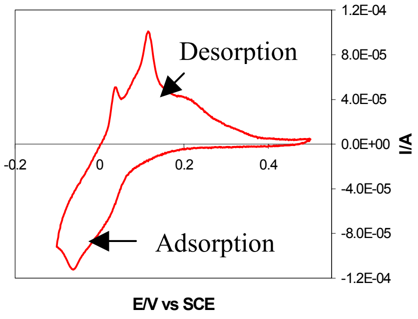
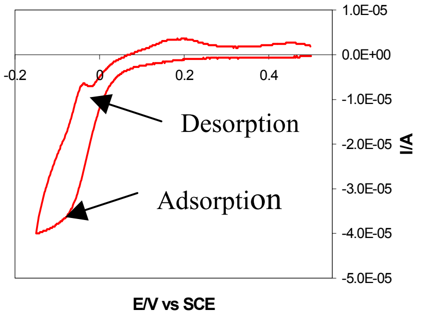


Figure 3: CV of Cu deposition on a BTSAM modified Au(111) surface (XAS Cell)



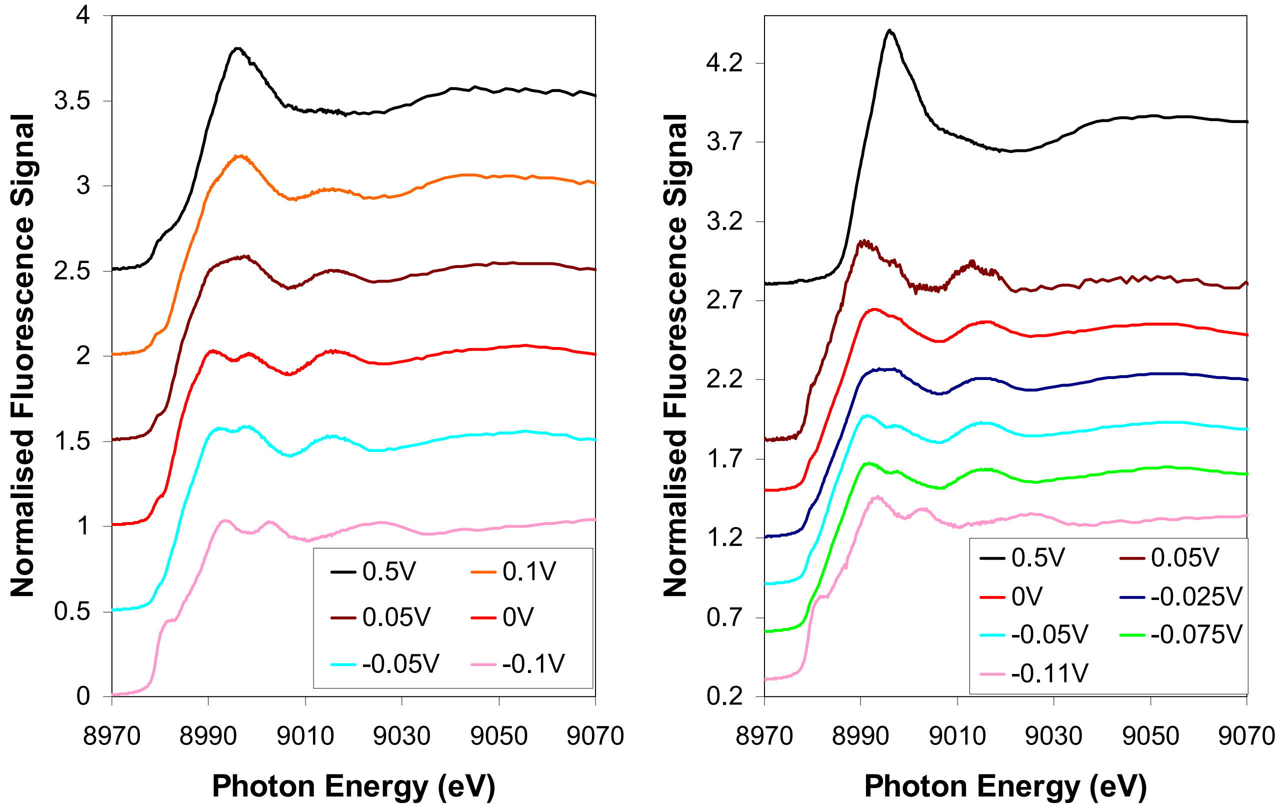
Prior to electrolyte withdrawal, cyclic voltammograms (CVs) were measured, (figure 2: bare Au(111) surface, figure 3: butanethiol SAM modified Au(111)) to provide an estimate of monolayer concentration and surface quality, followed by a period of 30min during which the potential was maintained at a chosen value to provide a well-ordered monolayer. Peaks in the CVs correspond to adsorption (lower half – cathodic sweep) and desorption (upper half – anodic sweep) of Cu. Repair of the single crystal Au(111) was achieved via chemical etching (KI/I_2 in aqueous solution) followed by flame annealing in a hand-held propane/butane torch and cooling under $N_2(g)$ stream. In the instance of the modified electrodes, the cooling preceeded immersion of the electrode in a 10mM solution of butanethiol in ethanol for a period of not less than 90min to establish the SAM.

XANES Analysis

The development of the XANES region for Cu electrodeposited onto both the bare and SAM modified Au(111) surfaces, with reduction of applied potential, is demonstrated in Figure 4. Inspection of the spectra provides an encouraging comparison between the bare and thiolated surfaces. At more oxidising potentials

(500mV vs SCE [Saturated Calomel Electrode]), it may be seen that the edge region for both surfaces has the appearance of Cu in solution (co-ordinated by six water molecules). By 50mV vs SCE, the Cu deposited onto the unmodified Au provides a spectrum which displays the beginnings of the characteristic double peak feature of a UPD monolayer at the edge. At 0mV, this feature is pronounced and by -50mV, the XANES region has a similar form to that of the bulk (metallic) deposit at -100mV.

Figure 4: XANES spectra for Cu UPD on bare Au(111) (left) and BTSAM modified Au(111) (right) electrode surfaces



In contrast, the electrode modified with BT-SAM exhibits no comparable indicator of monolayer formation until the potential reaches 0mV vs SCE. This is 50mV below that of the reference system. Thus, the thiolated overlayer forms a barrier to the UPD process, as predicted by CV measurements which reveal more reducing deposition potentials for the SAM/Au(111) interface. As the potential is reduced further, a distinctive double peak feature, dissimilar to the signal from bulk Cu or a monolayer of Cu on the bare Au(111), is established and maintained until -75mV. Relative surface concentration was measured simultanously as the difference in post and pre-edge fluorescence photon counts reaching the solid state detector; no significant variation in concentration was observed for these spectra (until the bulk deposit was reached). Such a range of potential over which the SAM/Cu(UPD)/Au(111) interface resists change is indicative of the stability of this arrangement within the electrochemical environment. In addition, a signal attributed to bulk metal formation is not obtained until -110mV vs SCE, well below the potential originally expected.

A shift in edge position can be seen for both systems as the applied potential is reduced. The 'solution' (Cu^{2+}) and 'bulk' (Cu^0) type spectra display characterisitic positions of 8987 and 8981eV respectively, whereas an intermediate shift to ca. 8983eV is present for the 'UPD' spectra. This implies that the Cu atoms in the monolayer retain a positive charge, although sufficient charge transfer from surface to adlayer occurs to create a chemical bond. We estimate that the oxidation state is approximately Cu^+ since the edge position is close to the metallic value (both d^{10}), although we are reluctant at this time to assign a transition to the edge due to the complexity of the local structure around the Cu adatoms.

EXAFS Analysis

For the purposes of structural modelling of the EXAFS, multiple spectra were combined to improve the signal to noise ratio; typically, two to four XAS spectra were added for each potential (40min/spectrum). Although this approach allowed well-defined oscillations to be observed to 300eV beyond the edge in the raw spectra, the level of noise was too high for meaningful fitting beyond $k = 10Å^{-1}$. The number of independent points (and therefore number of atomic shells) allows only 4 sets of atoms to be used to comprise the local environment of the Cu atoms for the computer generated model EXAFS. It is conceivable that the collection of further spectra would enhance the useable range of data (and therefore permit expansion of the structural model), but due to time constraints, this was not possible. The fact that only two spectra were required for in depth structural analysis is a testament to the excellent performance of ID26 for measurement of low concentration samples.

Initially, the 'UPD' spectra (for the two separate systems) were fit with 'standard' models, including Cu^{2+} in solution (octahedrally co-ordinated with H_2O) and Cu metal (fcc), which had been shown to give very low R (20-25) values for the reference samples, without any significant success. A wide variety of models, based on the concept of Cu sitting in 3-fold hollow, 2-fold bridging or atop sites on the Au(111) surface, with further co-ordination provided by oxygen and sulfur (sulfate counter ion) or sulfur and carbon (from the butanethiol), dependent upon the spectrum under investigation. The polarisation of the incident X-ray beam perpendicular to the electrode surface was included in the fitting and full multiple scattering paths were used in all models.

When comparing the quality of fit obtained between the two types of surface, consideration should be given to the fact that the Cu UPD onto plain Au(111) was also used to optimise the experimental arrangement within the hutch of ID26. Hence, the detector was often closer to the sample for the thiolated surface than the bare and the quality of data (and therefore value of R) is improved. This should not be taken to mean that the quality of model is higher for either type of sample; values are provided for comparison at different potentials within the same surface type.

(i) Cu UPD on Bare Au(111)

For the EXAFS spectra presented which have 'UPD' character, the 3-fold hollow model consistently provided the best fit to the real data. Although the investigation of this data is not absolutely complete, clear trends are observed as the potential is reduced from 100mV to -50mV vs SCE. The quality of the match increases since the fit factor, R, drops from 45.5 to 40.0 (figure 5: EXAFS fit for 50mV spectrum). In addition, the Cu is co-ordinated by three oxygen atoms, which sit directly above the Au surface atoms comprising the three-fold hollow arrangement, but the angle they subtend with respect to the surface normal, θ, reduces from approximately 55 to 40^o. At 100mV and 50mV, this provides a reasonable comparison with the structure proposed by Toney *et al.* using Grazing Incidence X-ray Diffraction (GIXD), which has sulfate ions bridging between the Cu atoms to form an ordered overlayer. In fact, including sulfur backscatterers rotated by 30^o in the surface plane relative to the oxygen shell gives a small improvement in the fit for all of the spectra.

The decreasing value of θ for the first shell of oxygen atoms implies a compression of the Cu on the surface of the electrode, perhaps due to the increasing concentration accompanying the formation of a full (1x1) monolayer. Indeed, there is a small increase in the difference between post and pre-edge fluorecence counts collected at 50mV and -50mV vs SCE accompanying this change. XAS measurements with the polarisation of the incident X-ray beam in the surface plane were attempted to assist in this assignment, but insufficient time was available to optimise the experimental arrangement in the hutch. Typical radial distances for the first four shells in our models are included in table 1.

Figure 5: EXAFS comparison for bare Au(111) at -50mV

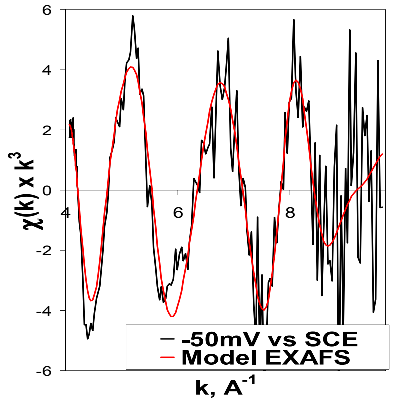
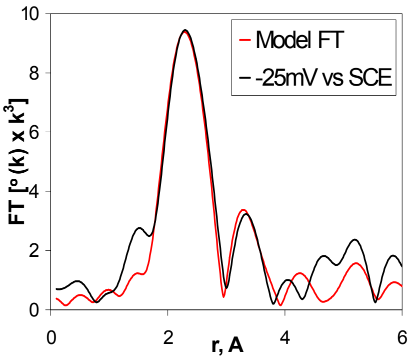


Table 1: Typical model parameters for bare Au(111)

Shell	Type	r (Å)	θ (°)
1	O	1.88-1.96	55-40
2	Au	2.58-2.70	143-137
3	S	3.35-3.40	50-40
4	Au	3.70-3.80	130-126

Figure 6: FT comparison for BTSAM modified Au(111) at -25mV



(ii) Cu UPD on BTSAM Modified Au(111)

Good quality fits were attained for the full range of potentials at which the spectra displayed 'UPD' type appearance. Two separate models provided comparable agreement with the real data at all potentials from 0mV to -75mV vs SCE: in each case, the Cu atoms were co-ordinated by a single sulfur atom (from the head group of the thiol), but the local arrangement on the Au(111) substrate varied with the adatoms located in either the 3-fold hollow and 2-fold bridging positions. Ultimately, the 3-fold bridging model is deemed the more appropriate structure, since the bridging site requires significantly higher Debye-Waller factors (disorder) for outer shells. A example of one of the fourier transforms (FT) obtained is shown in figure 6 (-25mV vs SCE) with the accompanying model.

The initial peak is actually created by the backscattering of both the first shell of Au atoms and the sulfur of the thiol chain, giving the peak an uncharacteristically high full-width at half-maximum (FWHM). The sulfur is typically 2.25-2.30Å from the Cu, which implies that it doesn't fully discharge, instead retaining some, or all of its negative charge. Further, each sulfur is found to sit above one of the three Au atoms comprising the 3-fold well (at $\theta = 45\text{-}55^{o}$), which would also place it in a 3-fold site on the Cu adlayer if it had formed a (1x1) arrangement on the substrate surface. Electrochemical concentration measurements lead us to believe that this is the case. Despite the similarities in the model structures for each of the potentials considered, it should be noted that there was a gradual improvement in the fit parameter ($R = 34 \rightarrow 29$) as the potential was dropped from 0mV to -75 mV. This implies a small increase in the degree of order of the interface at more reducing potentials.