**In-Situ X-Ray Techniques for Electrochemical Interfaces**

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**Abstract**

This article reviews progress in the study of materials by X-ray based techniques from an electrochemistry perspective. We are focusing on *in-situ/operando* Surface X-Ray Scattering and X-ray absorption spectroscopy and the combination of both. The background of those techniques together with the key concepts will be introduced. Key example of in-situ and in-operando investigation of liquid-solid and liquid-liquid interfaces are presented. X-ray scattering and spectroscopy have helped to develop an understanding of the underlying atomic and molecular processes associated with electrocatalysis, electrodeposition and battery materials. We will highlight recent developments including resonant surface diffraction and time resolved studies.

**Keywords**: Electrochemistry, Surface X-Ray Diffraction, X-ray Absorption, Spectroscopy

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# Introduction

At the electrochemical interface the structure, morphology and composition of the electrode surface and adjacent electrolyte can change when electrochemical processes take place. Structural rearrangements of the electrode including relaxation and reconstruction phenomena depend on several factors such as adsorbates, either from the electrolyte or as intermediates in a reaction, as well as the electrode potential and can alter growth behaviour during electrodeposition and affect electrocatalytic processes.

First insights of changes in the atomic surface structure and chemical composition related to electrochemical processes have been obtained from *ex-situ* UHV analysis (1-3) though results can be misleading due to changes occurring during the transfer from one system to another.

*In-situ/in operando* analysis with surface-sensitive techniques such as scanning tunnelling microscopy (STM) and synchrotron-based surface X-ray methods have made it possible to characterise the interface during electrochemical processes. In particular, surface X-ray diffraction (SXRD) permits to obtain extremely accurate crystallographic parameters for both, the metal substrate and suitable adlayers. The main elements favouring *in-situ* applications of X-ray based techniques are the considerable penetration depth of hard X-rays into water (or other solvents) and sufficient beam intensity from synchrotron sources which allows measurable scattering intensity from the surface region (4, 5).

An unquestionable advantage of X-ray based experiments is being able to obtain *in-situ* structural and spectroscopic information under potential control without disturbing the system. *In-situ* surface X-ray diffraction and X-ray absorption (XAS) techniques can provide detailed structural and spectroscopic information during *e.g.* adsorbate formation, electrocatalytic reactions and electrochemical phase formation on both the electrode and electrolyte side of the interface. X-ray structural characterisation permits structure analysis, as lattice parameter and phases, atomic position and site occupancy, strain/relaxation whilst X-ray spectroscopy allows to study chemical composition as valence state, coordination environment and bond distances and can give insight on the chemical state of specific atoms. A combination of those can help to develop a full picture of working electrochemical interfaces, as has been applied for battery materials (6-9).

Due to inherent low intensity of the scattering signal from the interface and the requisite of tuneable energy of the incoming X-ray for spectroscopic, the experiments required to be performed at Synchrotron light facilities.

The continuing development of synchrotron light technologies, including more intense and focussed X-ray beams, and the development of faster X-ray detectors covering larger areas has allowed *in-situ* X-ray techniques to be commonly employed and to develop beyond providing static spectroscopic and structural measurements.

In this article we aim to give an overview of the different types of X-ray scattering and absorption spectroscopic techniques and the information they can provide.

This work highlights the possibilities X-ray based structural and spectroscopic techniques offer to study electrochemical systems in-situ and in-operando obtaining insights into electrochemical processes and structure-activity relationships not accessible with other techniques.

A full coverage of the literature of those techniques applied to electrochemistry is not the scope of this article, we highlight specific examples and developments to give the reader an idea about the possibilities these techniques offer. Even though X-ray imaging and photo emission (10-13) are powerful techniques to study the electrochemical interface, they are beyond the scope of this article and we refer the reader to existing literature for further details. Moreover, we highlight recent developments, allowing to follow *in-situ* structural and chemical changes at the electrochemical interface in order to obtain more detailed information about the underlying electrochemical processes on a faster timescale, now being able to follow structural and chemical changes with millisecond resolution.

# X-Ray Scattering and Diffraction

In the following we are describing the basics of X-ray scattering and diffraction to be able to discuss specification and limitations arising from their nature. For a more thorough derivation and detailed description we refer the reader to existing literature (14-17). The intensity distribution resulting from the X-ray scattering might be thought of as a map in momentum (reciprocal) space, where the intensity is mapped as function of the reciprocal space coordinate I(**Q**). The scattering vector or momentum transfer **Q** is defined by the difference between the wave vectors of the incoming (**Qin**) and scattered (**Qout**) X-ray beam (**Q=Qin-Qout**) and is thus defined by the diffraction geometry (the sample and detector position with respect to the incoming x-ray beam) as depicted in Figure 1. The incoming X-ray beam scattered at each individual atom or ion results in a scattering amplitude described by an atom specific scattering factor *f* (**Q**, E).

The intensity distribution resulting from the scattering of all atoms is the square of the interference function obtained by summing the individual scattering contributions from each atom I(**Q**,E)= |, with *rj* the position of the individual scatter *j*.

The interference function reflecting the periodic distribution of the atoms in the crystal, gives rise to the diffraction pattern with discrete intensity spots in reciprocal space, the Bragg reflections. Notice that we always refer to measurements in the space of the reciprocal lattice, not in the real space of the crystal itself, this is the formalism used in crystallography and diffraction physics. The positions of any point in reciprocal space defined by the scattering vector *Q* can be described with reciprocal space coordinates called Miller indices *H*, *K* and *L (similar to assigning an x, y and z coordinate in real space)* **Q**=(H,K,L) (15).

The information we can access in real space depends on the choice of the length and orientation of the Q vector in reciprocal space. The length scale or resolution in real space is inverse proportional to the length of the Q vector and the structure contributing to the scattering is perpendicular to the reciprocal space vector. Therefore, we will divide the techniques in the following by their sensitivity to different aspects of the interface defined by the geometry employed (Figure 1), namely Surface X-ray Diffraction (SXRD), Reflectivity or Specular measurements (XRR) and Grazing Incidence Small Angle X-ray Scattering (GISAXS).

## Surface X-ray diffraction for electrochemical interfaces

The abrupt truncation of the electron density on the surface leads to the scattered intensity appearing in perpendicular direction to the surface (along the Qz or L direction as depicted in Figure 1) with an in-plane spacing representing the real pace in-plane atomic distances through Bragg’s law, thus we find the diffraction pattern to be a lattice of rods (14). These rods, called crystal truncation rods (CTRs) since they arise from the crystal being truncated, are the key characteristic of diffraction from surfaces and the intensity distribution along these rods can provide detailed crystallographic structural information on the atomic scale with high accuracy on relaxation (18-21) and roughening parameters (20, 22).

The sensitivity of the CTR to surface coverage and composition is demonstrated for monolayer of underpotential deposited Ag onto Au(111) in Figure 2a. In addition, the calculated CTR profiles for an ideal clean Au(111) surface (green), a full Ag monolayer on Au(111) (red), and a Ag bilayer on Au(111) (blue) demonstrate the sensitivity of the data to structural surface changes. (23)

Additional scattering from a reconstructed surface or ordered adsorbate adlayers with different lattice parameters from the bulk crystal lead to additional rods(24-26). The additional intensity streaks in reciprocal space and modulation of the X-ray scattering intensity from the surface due to the perceived change in coverage of the first atomic layer, adsorbate layers (24, 25), underpotential deposition (27-31) and reconstructions (25, 26, 32) were the first systems to be studied by surface x-ray diffraction. The intensity distribution for a change in the surface periodicity is shown in Figure 2b as a schematic for the example of the Au(111) reconstruction around the (0, 1, 0.5) CTR position (solid symbol) indicating the peaks that arise due to the surface reconstruction (open symbols).(33) The corresponding contour map I(h,k) map of the measured X-ray intensity in the l = 0.5 plane at the same position is also shown.

Those studies have provided valuable insights into coverage, relaxation, adsorbate structures, bond lengths and their dependence on the applied potential.

Potentiodynamic measurements, when the scattered X-ray intensity is measured while the electrode potential is cycled over a potential window or stepped between two potentials can give valuable information about reversible and irreversible potential dependent structural changes, electrode stability and the dynamics of electrochemical processes. As an example the changes observed while scanning the potential are shown in Figure 2c for Ag underpotential deposition on Au(111) at different points in reciprocal space on the specular CTR at (0 0 1.5) and the two non-specular CTRs at (1 0 3.7) and (0 1 0.5) sensitive to relaxation effects and surface coverage, respectively.(23) Reversible processes studied include the lifting of the reconstructions on Au (26, 32-37) and Pt (38-40) surfaces, elucidating the role of the surface charge and adsorbed species. Potential step experiments, monitoring the intensity while stepping the potential permit to record intensity transients as shown in 3d for the copper underpotential deposition on gold allowing to deduct time constants for structural changes. (41, 42)

In addition, surface X-ray diffraction has played a key role in elucidating structural changes due to possible adsorption and/or absorption of species involved in electrocatalytic reactions (43), e.g. CO adsorption and oxidation on platinum could be followed on Pt(111) (44). More recently the subsurface adsorption of oxygenated species on Pt (45-49) and Cu (20) could be studied.

Studies of bulk alloys have helped to follow *in-situ* structural changes during corrosion (50-53) including the formation of a thin passivation layer followed by the formation of substrate islands at larger overpotentials, this behaviour is altered in the presence of halides (54).

Other potential induced processes which are well suited for the study by X-ray diffraction are the electro-dissolution and electrodeposition at single crystal electrodes (55-58). Due to the changes in roughness and morphology of the crystal surface upon deposition or dissolution measurable intensity changes can be observed. The scattered intensity is monitored at selected reciprocal space positions as a function of time while depositing on the electrode surface which allows to follow different growth modes and establish the influence of potential adsorbates and additives on those (56, 58, 59).

Data acquisition rates with time resolution of millisecond are achievable as has been shown for the electrochemical dissolution of Au(001) in Cl-containing electrolyte (60).

A drawback of the use of X-ray diffraction to study electrochemical processes is the limited reciprocal space that is accessible with the use of point detectors. Usually only one point in reciprocal space can be studied and changes of the interface which would be possible to observe at different places in reciprocal space remain uncovered, thus not allowing to obtain information of a larger region and to follow several processes simultaneously. When studying the influence of adsorbates onto the electrodeposition on copper for example the roughening of the surface giving insight into the growth mode and the signal coming from the adlayer, giving insight into the adsorbate structure and coverage, had to be recorded in two different sets (56).

Modification of the experimental conditions are required to overcome this limitation. The use of high energy (smaller wavelength) X-rays, thus compacting the reciprocal space and allowing to monitor a larger region with one 2D detector simultaneously has been employed over the recent years (45, 46, 61, 62).

Another approach to obtain information of more than one point in reciprocal space is the use of dispersive X-rays in combination with a 2D detector. In this case the incoming beam uses a multi-wavelength instead of using X-rays of single energy (63-65). With the absolute value of the scattering vector ***Q*** being proportional to the inverse of the wavelength λ of the X-ray beam |***Q*|**~1/ λ a range of ***Q*** vectors is instantly accessible. Instead of having to adjust the scattering angle the intensity distribution observed corresponds to a range of ***Q*** and a CTR profile is observable with millisecond time resolution, allowing to study structural change of electrode surface layers (63).

Perhaps the main disadvantage that still remains is that SXRD is limited to well-ordered single crystal surfaces studies and cannot, up to the date, be applied to nanometre sized particles, although with the developments of the techniques such as GISAXS and EXAFS this problem has been overcame as exemplified in following sections.

## Reflectivity/specular measurements

Reflectivity can be considered as a subset of surface X-ray diffraction with the limitation of the ***Q*** vector being normal to the surface plane (***Qinplane***=0) thus monitoring structural changes perpendicular to the surface plane not requiring a specific in-plane symmetry. Quantitatively, XRR is sensitive to the surface normal electron density profile. When combined with surface X-ray diffraction the CTR with the limitation of ***Qinplane***=0 is called specular CTR and the information obtainable is similar to the one for reflectivity measurements. Reflectivity measurements can be achieved by varying the incident and exit angle with the restriction that the exit angle is the same as the incident angle at all times (Figure 1). The method thus investigates any structural changes normal to the interface and can be useful specifically to systems which do not have an in-plane symmetry *e.g.* are not sensitive to restructuring within a surface plane.

For electrochemical interfaces reflectivity and specular measurements have been employed to study the ordering of the ions close to the interface both for electrodes with in-plane symmetry and for electrodes without any crystalline structure, such as liquid-liquid interfaces. A detailed description of scattering from liquid interfaces can be found in reference (66). Characterisation of polarisable liquid/liquid interfaces via X-ray scattering have been conducted both for interfaces between an organic and aqueous electrolyte and between a liquid metal and aqueous electrolytes (67). For the mercury-aqueous interface a pseudo-Bragg peak was observed, indicating surface-adjacent layering within the mercury phase which shows potential and temperature dependence (68). The potential dependence of the additionally observed surface roughness could be explained by a response of the free electrons to the applied potential (69). A nucleation and growth process at the mercury–aqueous showed the formation of a precursor followed by quasi-epitaxial 3D crystal growth, which was assigned to a combined action of electrostatic and short-range chemical interactions (70).

X-ray reflectivity has been used to study the ion distribution at the organic-aqueous interface (71-74). The results have allowed to obtain ion concentration profiles for different cations at various interfacial potential. These works further permitted to extract excess charges for different potentials and determine experimentally potentials of mean force for different ions. More weakly hydrated ions were found closer to the interface showing that the contribution of ion pairing to the free energy of adsorption is very small for the investigated ions (71). Furthermore, to quantitatively describe the ion distribution at the interface requires to take into account the interplay between ion–solvent interactions and ion–ion correlations (73). Other applications of reflectivity to liquid-liquid interface monitored the assembly of water-soluble, heavily charged nanoparticles into an interfacial monolayer located on the organic side of the interface (75) and the molecular ordering and phase behaviour of surfactants at the water-oil interface with sub nanometre spatial resolution as a function of depth into the interface (76).

Similar to the characterisation of a liquid-liquid interface, specular X-ray scattering/reflectivity can be employed to obtain information about the liquid structure at the solid-liquid interface (77). Employing the reflectivity or specular rod in combination with SXRD allows to separate the contributions coming from the ordered crystal (Figure 3a) from the effect of the liquid layering onto the intensity distribution to interfacial water structures. Attention has to be however paid to the contrast of the electron densities and the structure of the electrolyte. Layering gives rise as already discussed for liquid-liquid surface to so-called quasi-Bragg peak (Figure 3b, green line), which will show up as an intensity modulation asymmetric with respect to the Bragg peaks of the CTR. Electrolyte structures without specific layering represented by an error function are less easy to distinguish as the intensity modification will be at low L values (Figure 3 b, blue line) which is also the region where effects of the beam or detector footprint being larger than the sample and misalignments such as the beam not hitting the centre of the sample might affect the results.

One of the first electrochemical systems investigating the electron density of the electrolyte normal to the surface Ag(111) in 0.1 M NaF showed a clear potential dependence of the ordering in the electrolyte. The presence of a dense ice-like layer of water adjacent to the interface and the flipping of the water molecule dependent on the applied potential was proposed (78). This was followed up by a more recent study of Ag(111) in 0.1 M KOH; the non-specular and specular CTR were measured. The changes with potential on the specular CTR are more pronounced (Figure 3c) and were assigned to electrolyte effects in addition to changes in the relaxation. A layer of hydrated K+ cations in the outer part of the double layer at the negative potential end was proposed (shown in Figure 3d, left). At the positive potential end adsorbed OH stabilising a hydrated K+ cation layer through non-covalent interaction thus forming a compact double layer structure in with a reduced Ag-K+ distance was found (Figure 3d, right). (79)

Timer resolved measurements of the specular CTR as shown in **Error! Reference source not found.** gave insight onto transitional structures during underpotential deposition of various metal cations on Au(111). (41) The intensity transient obtained for different copper concentration allowed to deduct the kinetics and time constants of adsorption (**Error! Reference source not found.**d). In general, the adsorption rate of the metal cations is related to the coordination energy of solvation.(41)

More recent studies investigated the atomic-scale interfacial structure of a non-aqueous liquid electrolyte solution with implication for Li-ion batteries. The roughness of the electrode was found to have minor effects on the interfacial structures. The solid interface gives rise to liquid layering near OCV and determines the orientation of the electrolyte molecules and ions near the surface electrolyte does not follow the structureless diffuse electric double layer predictions of the Gouy–Chapman model. The interfacial structural properties are mainly governed by specific intermolecular interactions, such as van der Waals, Coulomb and dipolar, rather than being governed by specific substrate–molecule interactions (80).

One of the disadvantages in scattering techniques is the phase loss of the complex structure future due to the intensity being proportional to the square of the scattering factor I(***Q***,E)= |. This means that a direct retrieval of the atomic positions is not possible and structural information relies on atomistic models to be refined through iterations. Analysis of the specular CTR through a non-iterative approach has recently been developed (81) this is possible for the specular CTR only as the data close to the origin of the reciprocal space (Q=0) is accessible and the intensity and electron density are continuous, thus related through causality. The approach has been applied to retrieve the electron density of the ion layering and monitor the Stern layer behaviour on Pt(111) (82) and RuO2(110) and RuO2(100) (83) as a function of potential.

## Small angle scattering/diffuse scattering

Grazing incidence small angle X-ray scattering (GISAXS) (84, 85) can be employed, often in combination with atomic scale methods, to obtain *in situ* and *operando* information on the nanoscale in electrochemical environments for both solid-liquid and liquid-liquid interfaces. The wavevector is typically between 0 and 1 nm-1 thus allowing large dimensions typically in the order of a few nm to a few hundreds of nm in real space to be probed. A representative GISAXS setup for electrochemical studies is shown in Figure 5a.

Thus, information about morphology and nanoscale objects perpendicular and parallel to the surface can be obtained.

The potential dependent study of nanoparticles at an aqueous organic is an example of using X-ray methods to follow the ordering of nanoscale objects. An arrangement of the particles into a hexagonal lattice over the investigated potential range was observed showing potential-dependent changes in lattice spacing and in-plane correlation length (75).

Due to the small range in reciprocal space to be covered, the diffuse scattering in the near forward direction, GISAXS employed with a 2D detector allows to follow changes at the interface on a fast time scale only limited by the signal-to-noise ratio and frame rate of the detector.

Examples include following growth processes during electrodeposition which lead to a change in the surface morphology and to monitor the kinetic roughening during the initial stages of electrodeposition. For Au(001) surface in chloride containing electrolyte, intensity maps at various times *t* of a growth experiment on the unreconstructed Au(001) surface are plotted as a function of the in-plane scattering vector components qx and qy (Figure 5 b) allowed to fit the line profiles (Figure 5c) in order to extract the peak position qr as a function of deposition time. This gave insight into the lateral mound size as a function of deposition time for various deposition potentials during the 3D growth (86) .

Quantitative study of the structural evolution of Pt(111) in HClO4 during oxidation/reduction cycles showed a coarsening of the formed nanoscale 3D islands with the number of cycles. The morphological evolution in the electrochemical system strongly resembles that found in homoepitaxial growth under UHV conditions (47).

GISAXS allows to follow morphology changes including roughening processes on a fast time scale. The structure of Pt(111) a place exchange of Pt and oxygen atoms was observed during surface oxidation . The resulting oxide consists of an oxygen rich outer and a Pt-rich inner atomic layer but approaches a more uniform stoichiometry with increasing potential the oxide (46).

# X-ray Absorption Spectroscopy (XAS)

So far, we have focused on samples with long range order which can be probed by diffraction methods. In contrast, X-ray Absorption spectroscopy can be employed to obtain structural and chemical information from samples without requiring long-range order including amorphous materials and nanoparticles (87), but can also provide additional information for crystalline surfaces. The change in the X-ray absorbed by the sample while the X-ray photon energy is varied from below to above an absorption edge of a specific element is monitored and gives information about the near range structure and chemical environment of the probed atom (88, 89).

The XAS spectrum is divided into two regions with defined energy relative to the absorption edge and revealing different information about the local environment and the absorbing atom itself. X-ray absorption near edge structure (XANES) covers energy ranges up to several tens of electron volts (eV) above the edge and is directly linked to the electronic configuration and sensitive to the oxidation states of the atom probed (90). The extended X-ray absorption fine-structure (EXAFS), which extends from 50 eV above the edge to 1000 eV, approximately (91), arises from the backscattering of the photoelectron and thus contains information about the local environment of the absorbing atom including the chemical environment and nearest neighbour distances.

In electrochemical environment the range of absorbing atoms is restricted by the X-ray energy able to penetrate the sample and/or the electrolyte with absorption energies typically >5 keV thus in this specific environment not allowing to study elements with low atomic number. *In-situ* XAS can provide information about the chemical composition and oxidation state of individual elements in a multi element material, allowing to monitor chemical and structural changes during redox processes. This is of particular interest and has been employed to the study of materials and reactions for energy processes such as CO2 reduction (10), oxygen and hydrogen evolution reactions (92), fuel cells (93, 94), heterogeneous electrocatalysts (95) and nanoscale catalysis (96).

X-ray absorption spectroscopy is not limited to short range ordered samples and can be employed to single crystals. In this case surface sensitivity and depth profiling can be achieved by using grazing incident X-rays and by varying the incident angle of the X-rays, respectively. (97) This is especially useful when studying deposition of foreign metals such as underpotential deposition, as the element specificity allows to distinguish between surface and deposit and to detect disordered deposits and possible surface alloying and/or the coadsorption of oxygenated species (98-103). X-ray absorption techniques have been extensively reviewed and are commonly employed to probe changes in chemical properties and the local environment of specific sites during electrochemical reactions. We therefore aim here to only highlight few examples and recent developments to demonstrate its use to develop a further understanding of fundamental electrochemical processes and applications.

X-ray absorption spectroscopy has helped to build an understanding of the activity, selectivty and stability relationship of electrode materials for CO2 reduction by revealing oxidation states, coordianation number and atomic distances under reactive conditions.

Copper has been extensively studied (not only with XAS) as CO2 reduction due to its ability to bind CO while hydrogen underpotential deposition does not occur (104), thus being able to catalyse the CO2 reduction to hydrocarbons. X-ray absorption spectroscopy has helped to gain insights into the chemical changes occurring during the reaction by analysing the XANES part of the spectra and into the stability and oxide formation by extracting coordination numbers and atomic distances from the EXAFS part of the spectra not only for copper but also for copper alloys as shown as an example for  copper-complexes (105) and CuOx nano-cubes(106) in Figure 6.

The activity and selectivity during electrochemical CO2 reduction (107) reaction has been studied with *in-situ/operando* XAS for copper(II) phthalocyanine (CuPc), copper(II) benzene-1,3,5-tricarboxylate, and copper(II) 1,4,8,11-tetraazacyclotetradecane chloride ([Cu(cyclam)]Cl2). Among those complexes, CuPc shows the highest activity and selectivity for electrochemical CO2 reduction to CH4. The observed XAS spectra while stepping the potential from open circuit voltage to the potential for electrocatalytic reduction are shown in Figure 6a. The XANES analysis reveals a formation of Cu(I) followed by Cu(II) during this process. The Fourier transformed EXAFS shown in Figure 6b allowed to follow the change in bond distance and coordination numbers during the potential change. The formation of Cu-Cu bond with a length of 2.2 Å can be observed under operating conditions accompanied by a decrease in the Cu-N and Cu-C coordination number associated with CuPc and increase in the Cu-Cu coordination number (Figure 6 c). The change in oxidation state was found to be reversible only for the CuPCc complex.

XAS data obtained from CuOx nano-cubes has been obtained approximately every 10 minutes (Figure 6d). The XANES data (inset in Figure 6d) reveals a change in the pre-edge feature indicating a change of the chemical state of copper towards metallic copper. The change in the local environment of the copper atoms could be extracted from the EXAFS. The Fourier transformed EXAFS (Figure 6e) shows a change from the Cu-O distance towards a Cu-Cu bonding length, which is accompanied by a change in coordination number for Cu -O from 2 to 0.3 and for Cu-Cu from 3.6 to 12. The expected coordinated number for Cu-Cu in a bulk distance is 12, thus the copper atom is during this reaction undercoordinated. For copper nano-cubes a coordination number of 10.8 was obtained for the Cu cubes indicating the formation and growth of pores on the Cu cubes under reaction conditions leading to an increased surface roughness.(108)

The relative concentration of the metallic copper and copper oxide as a function of time during CO2 reduction are shown in Figure 6e. The reduced coordinate number under reactive conditions accompanied indicate an induced copper roughness during the reduction of the copper oxide electrode during the loss of oxygen. Under reactive conditions, the surface and the bulk of the electrode are dominated by the existence of reduced copper, which correlates with enhanced C–C bond formation at higher cathodic polarization due to the increased metallicity of the copper electrode (109)

Interestingly, in comparison in-situ XAS revealed that Zn (II) centre maintains its oxidation state under reaction conditions, which means that the Zn centre does not experience a redox reaction but CO2 reduction driven by the ligand.(105)

Oxygen evolution reaction (OER) has also been broadly studied by XAS (110-114). The atomic-level structure of Pt3Ni nano-frame catalysts could be identified and linked to differences in their oxygen reduction reaction activity showing that nano-frame surfaces with different structure exhibit varying levels of binding strength to adsorbate molecules (111). The role of oxygen during the OER in an electrodeposited Ni-Fe(OxHy) electrocatalyst was investigate in the soft and hard X-ray regimes in alkaline pH (112). Multi-metallic oxide electrocatalysts exhibits impressive oxygen reduction activity in alkaline fuel cells. *In-situ* XAS resolved the synergistic catalytic mechanism of bimetallic oxide such as Co−Mn oxide catalyst (113) and to understand even more complex systems as trimetallic oxides (Mn-doped cobalt ferrite) under real-time fuel cell operating conditions (114).

Although only the local environment of the specific atom type is involved, XAS allows to probe the local geometric ligand environment and electronic metal states of oxygen-coordinated iridium centres in nickel-leached IrNi@IrOx metal oxide core–shell nanoparticles under catalytic oxygen evolution (115).

In situ EXAFS has been used to study the electrochemical formation and electrocatalytic activity of core shell nanoparticles, allowing to follow the potential dependent changes in coordination number and oxidation state by recording spectra of the elements of the core and shell separately. The formation of core shell nanoparticles was followed by EXAFS studies during the underpotential deposition of Cu onto a carbon-supported Au electrocatalyst investigating the initial stages of formation of the core-shell (116). Different methods of depositing Au@Pd core@shell nanoparticles (117) have been studied. The formation of a potential induced hydride phase could be followed for a series of Pd@Pt core-shell catalysts with varying Pt shell thickness monitoring lattice and inter-atomic distances of the metal neighbour pairs (118).

Time-resolved XAS technique was applied to investigate the key factors that limit the rate capability of Li-based batteries for a Li1.2Ni0.15Co0.1Mn0.55O2 cathode following the contributions of the three different transition metals in the cathode to the electrochemical charge/discharge reactions. (119)

The investigation of kinetics and underlying mechanism of electrocatalytic systems *in operando* requires a high time resolution not achievable with standard XAS set-ups where one spectrum can take in the order of ten minutes. Quick EXAFS allowing to change the energy of the incoming X-ray beam much faster time-resolved compositional information for CO2 reduction on CuOx catalysts (120). Similar to X-ray the use of dispersive X-rays allows the whole X-ray absorption spectrum to be collected simultaneously enabling time-resolved XAS experiments on a time scale of milliseconds. The local chemical environment and electronic structure of iridium during the oxidation of Ir(III) to Ir(IV) in the water splitting process on electrodeposited iridium oxide films under chronoamperometric conditions in both acidic and basic media was studied this way (121).

# Combination of Spectroscopy and Diffraction

The combination of spectroscopic and structural X-ray techniques can be useful to get more concise information on the electrochemical interface. Diffraction techniques have the drawback that the only element specificity comes from the atomic scattering factor. Whereas EXAFS/XANES does have the disadvantage of being a bulk characterisation technique, the signal stems from the whole sample, thus not giving specific interfacial information. Specifically, for crystalline surfaces with elements that have atomic numbers which are close, (as the atomic scattering factors scales with the atomic number Z) those elements are indistinguishable by structural data. The application of anomalous or resonant scattering in which the energy of the incoming beam is scanned through an X-ray adsorption edge while the scattering vector ***Q*** is kept constant, can be useful to identify the specific phase and thus gain element sensitivity in the positional parameters. In the case of bi-metallic systems such as underpotential deposition (122-125) and alloy surfaces (50, 126, 127) the concentration profile at the surface in the electrochemical environment can be obtained.

In the same way resonant scattering allows to get element specific information reveal element-specific ion distributions to the electron density profile obtained from specular reflectivity (128, 129). The cation specific study revealed the distributions of mono-and divalent cations to be different which could be associated to a difference in their interfacial hydration structure. (130, 131) Studying the density profile as a function of ion concentration allows to develop a model for the concentration-dependent coverage and to deduct an effective surface charge.(132, 133)

Another advantage of resonant diffraction is that similar to XANES, the spectra contain information about the chemical state of the atomic contribution to the diffracted signal and thus allows to obtain sub-monolayer sensitive information of the oxidation states of the surface atoms. The electrochemical oxidation of Pt(111) single crystal surface was studies in this way (134, 135). It could be shown that the place exchange of surface platinum and oxygen is accompanied by second-layer platinum atoms losing their electrons to nearest neighbour oxygen atoms. Varying the polarisation of the X-rays between being normal and parallel to the surface plane of the electrode showed a strong dependence of the diffracted intensity on the polarisation angle (135, 136) which was attributed to anisotropic local environment of Pt surface atoms.

More recently attempts were made in quantifying the resonant surface X-ray diffraction signal and the polarisation dependence observed to probe the charge transfer between the metal electrode and the adsorbing species in the electrolyte solution.

Adsorption of halide anions Cl- and Br- onto Cu(001) (137, 138) and Au(001) (139-141) electrochemical systems were studied in order to directly probe the charge transfer and nature of the chemical bonding (142). Moreover, a theoretical tool based on an *ab-initio* approach to simulate surface resonant X-ray diffraction experiments is being developed (143) and allows to obtain details about the local electron density and bond formation from the resonant surface diffraction spectra.

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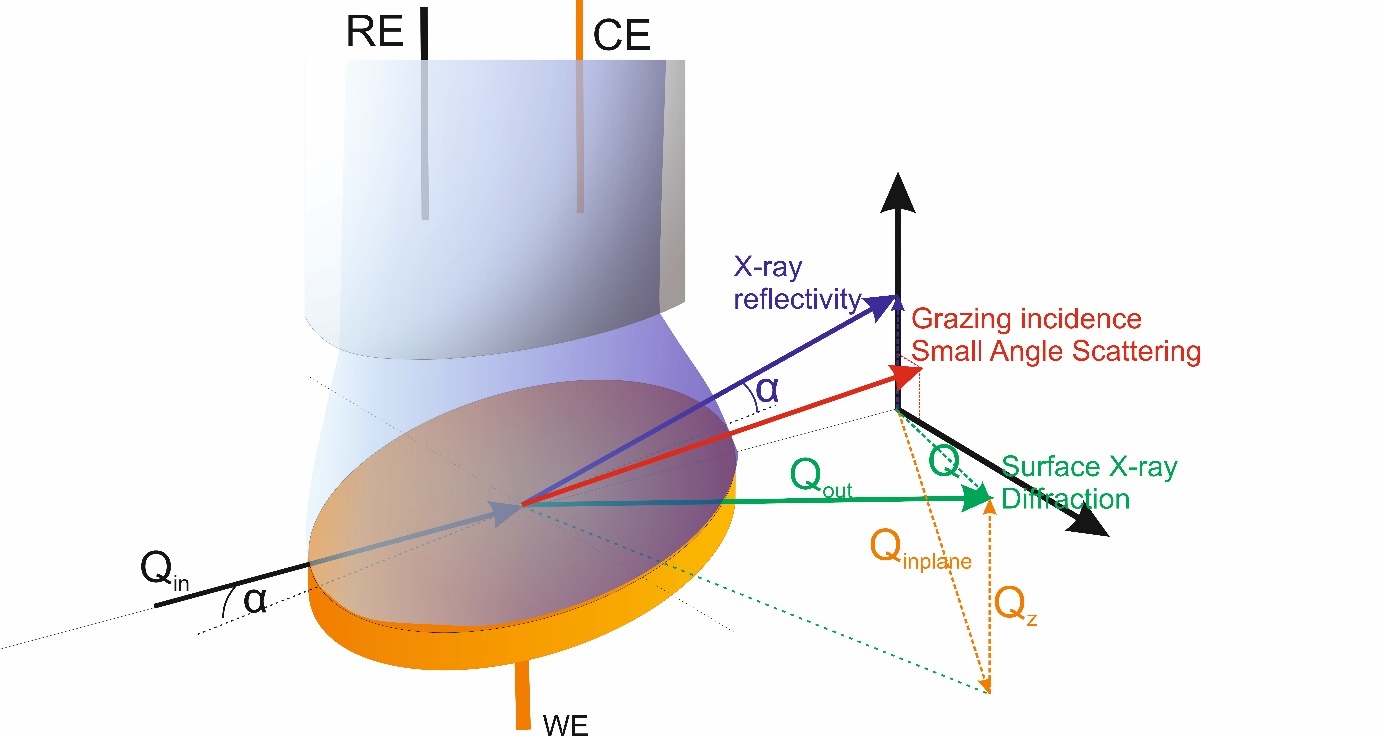
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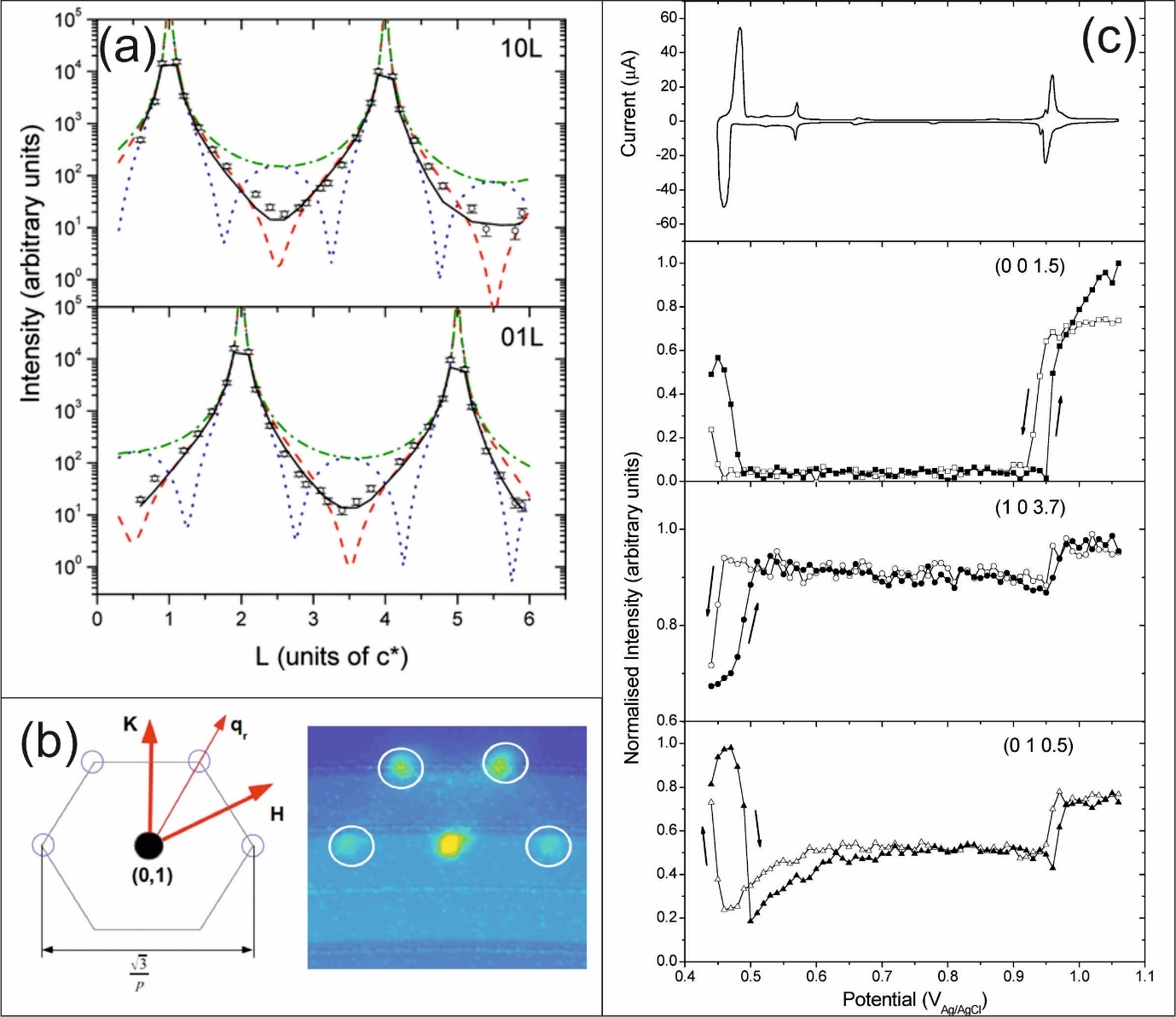
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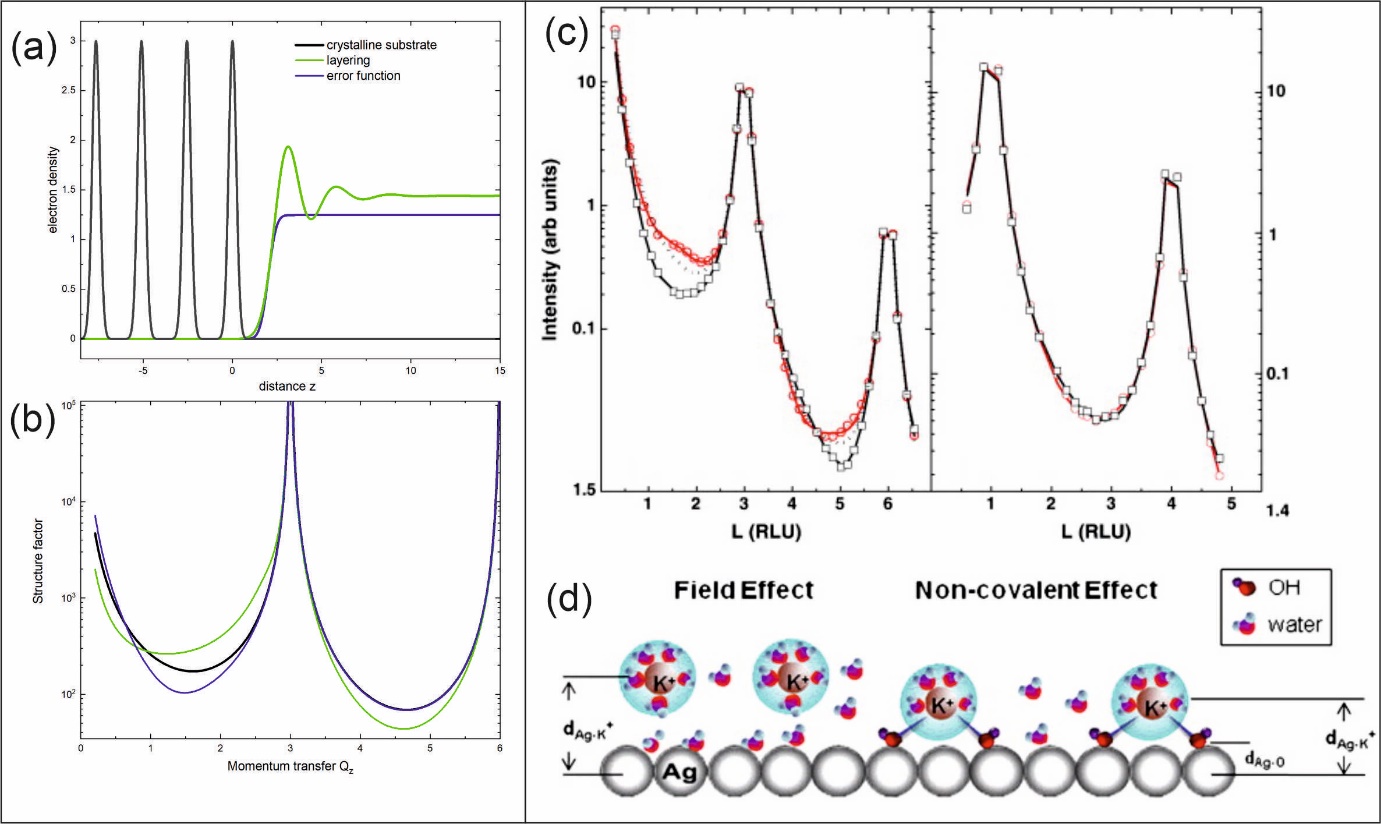
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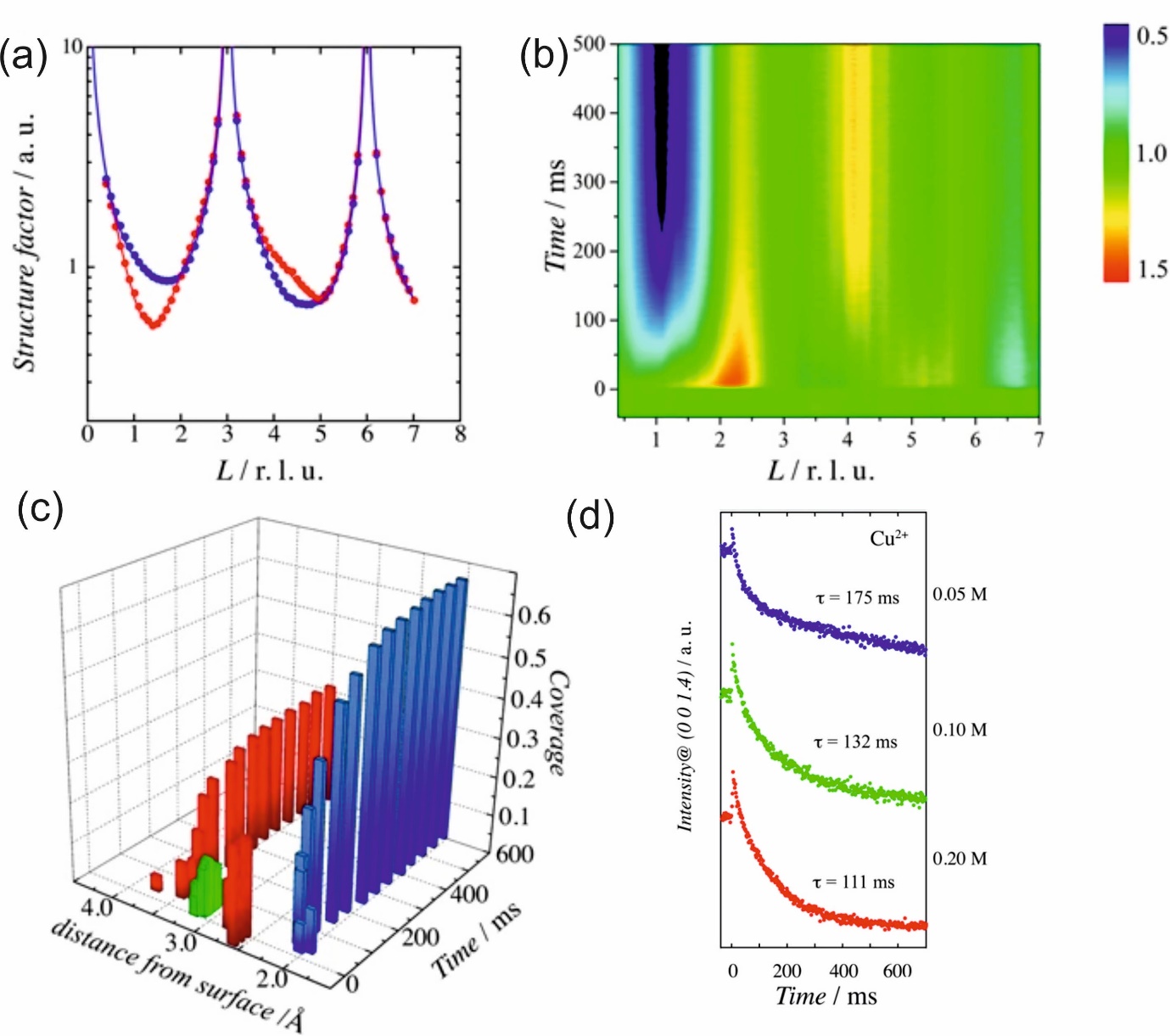
**Figure 1** Scattering and diffraction geometries for X-rays measurements probing a surface in an electrochemical cell are shown. The x-rays penetrate the electrolyte and the scattering form the surface is observed. The scattering vector **Q**, with **Q=Qin-Qout**, defines the structural position (through it’d direction) and length scale (through its length) to be probed. In this paper we distinguish between Surface X-ray diffraction, which is sensitive to structural changes with the same in-plane symmetry of the crystalline substrate on the atomic scale, X-ray reflectivity, with the Q vector perpendicular to the surface probing structural information perpendicular to the surface And GISAXS with the Q vector length being smaller than for the other two techniques, allowing to access structural information on the scale of nanometres.



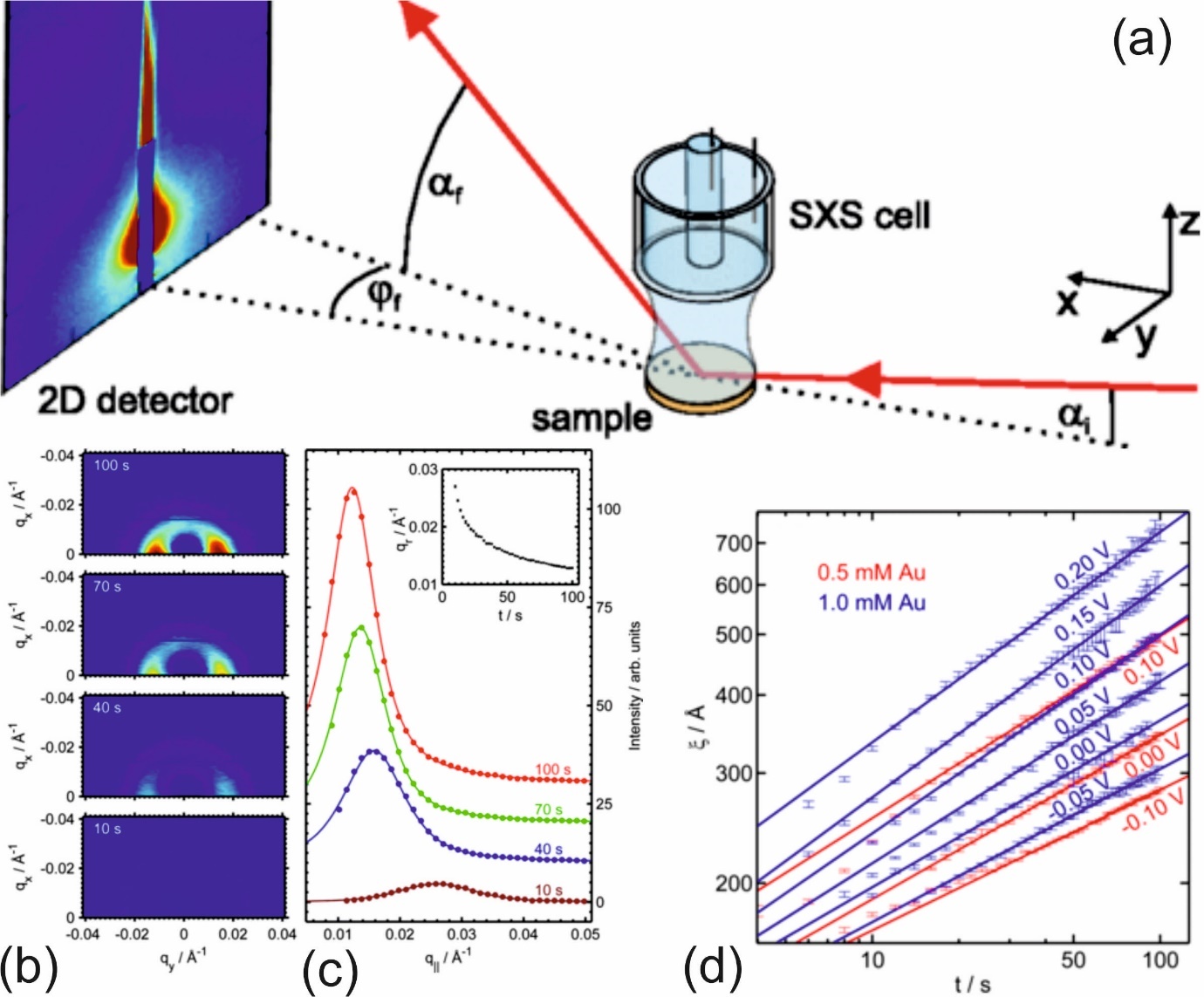
**Figure 2** The influence of surface layers of densities and/or symmetry different than the substrate is demonstrated (a) Crystal truncation rod (CTR) data (black circles) of a Au(111) electrode with 1 monolayer of underpotential deposited silver is shown together with calculated CTR profiles for an ideal clean Au(111) surface (green), a full Ag monolayer on Au(111) (red), and a Ag bilayer on Au(111) (blue).(b) A schematic of the scattering in the surface plane of reciprocal space around the (0, 1, 0.5) CTR position of a reconstructed Au(111) surface is shown together with together of a contour map of the measured X-ray intensity in the l = 0.5 plane of the same position. (c) Cyclic voltammetry of silver underpotential deposition on Au(111) together with the X-ray voltammetry measured at different reciprocal space positions. The potential dependent changes in the intensity do match the current peaks in the cyclic voltammogram and can be assigned to electrochemical processes of Ag deposition and adlayer formation and lifting. Figures 2a and 2c adapted with permission from (J. Phys. Chem. C 2016, 120, 29, 16100–16109). Copyright (2016) American Chemical Society from (23) and Figure 2b adapted with permission from Reference (33)



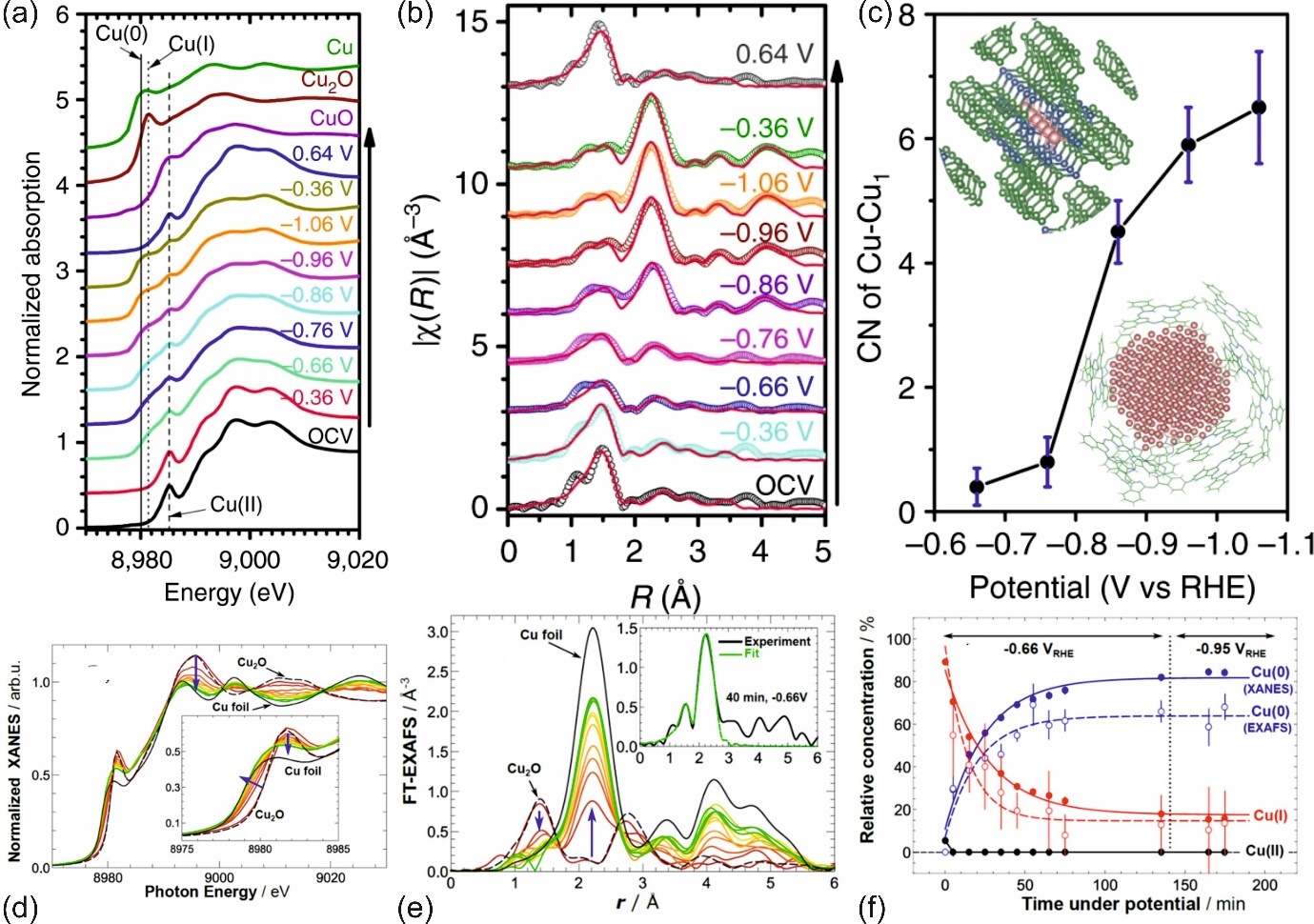
**Figure 3** The sensitivity of X-Ray Reflectivity to structure normal to the surface, here specifically the electron density of the liquid side of the interface is demonstrated by showing (a) the different components contributing in real space and (b) the contribution of the structure of the liquid onto the specular CTR showing the contribution of the substrate only, the homogeneous liquid represented through an error function and through a layered model. (b) the non-specular CTR (right) and specular CTR (left) of the Ag(111)/0.1 M KOH interface measured at − 1.0 V (circles) and − 0.2 V (squares) versus SCE. (d) The [interfacial structure](https://www.sciencedirect.com/topics/chemistry/interface-structure) at the negatively charged (left) and positively charged (right) surface obtained from modelling the data in (c). Adapted with permission from (79).



**Figure 4** The study of copper underpotential deposition on Au(111) with the help of specular CTRs is presented (a) Specular CTR of Au(111) at the underpotential deposition potential of 0.45 V (red points) and at a potential of 1.05 V at which no underpotential deposition occurs vs SHE (blue points). The solid lines are the structure factors calculated from the optimized models. b) The time–resolved specular CTR after the potential step from 1.05 V to 0.45 V with time resolution of 0.5 ms is shown. Red and blue regions indicate the increase and decrease of intensity, respectively. c) Time dependence of the structural parameters extracted by optimising a model to fit the data from (b) The blue, red, and green bars represent the underpotential deposited Cu, adsorbed (bi)sulphate, and non–adsorbed Cu, respectively. d) Intensity transients at the (0 0 1.4) position for different sulphate concentration were recorded with time resolution of 1.0 ms to follow the deposition process. Figure adapted from Nakamura (2017) (CC BY)(41)



##### Figure 5 (a) A typical setup for GISAXS (b) The intensity distribution I(qx,qy) obtained after 10s, 40 s, 70 s and 100 s after initiating 3D growth on an unreconstructed Au(001) surface and (c) the Corresponding radial intensity distribution I(q∥) (symbols). Lorentzian line shape fits (lines) to the data allowed to extract the peak position qr as a function of deposition time (inset) and (d) to extract the lateral mound size as a function of deposition time for various deposition potentials. Adapted with permission from (86)



**Figure 6** In situ XAS measurements under electrocatalytic reaction conditions. a) Cu K-edge XANES spectra, (b) Fourier-transformed Cu K-edge EXAFS spectra and (c) the extracted potential dependence of the coordination number for Cu-Cu for CuPc. (d) Cu K-edge XANES spectra, (b) Fourier-transformed Cu K-edge EXAFS spectra and (d) the extruded time dependence of the relative concentration of Cu(0) and Cu(I) under reactive conditions for CuOx nano-cubes. Figures 6(a-c) adapted from Weng (2018) (CC BY)(105) and Figure 6(d-f) adapted from Möller (2020) (CC BY) (106)