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NOTES AND INSIGHTS OPEN ACCESS

XPS Insight Note—Strategies for Obtaining Peak Shapes and Inferring Chemistry

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Received: 30 July 2025 | **Revised:** 21 August 2025 | **Accepted:** 29 August 2025

Funding: This work was supported by the Engineering and Physical Sciences Research Council (EP/Y023587/1), (EP/Y023609/1), (EP/Y023536/1), (EP/Y023552/1), (EP/Y023544/1).

Keywords: fitting | oxidation | peak shape | reduction | XPS

ABSTRACT

The chemical specificity of x-ray photoelectron spectroscopy (XPS) for the analysis of surfaces is well established. However, overlapping peaks and complex peak shapes can hinder routine analysis of spectra. Studies involving controlled changes to samples to systematically change photoelectron spectra can reveal invaluable information on peak shapes and hidden spectral features. This insight note is presented to educate users in embracing and utilising changes in spectra to facilitate spectral analysis.

1 | Introduction

In multiuser facilities, such as that run by the authors, the level of experience of its users with x-ray photoelectron spectroscopy (XPS) varies significantly. Consequently, understanding, yet alone interpretation, of photoelectron spectra can be difficult and has been highlighted widely in the literature [1]. Whilst training of the next generation of XPS specialists is required, the demand on the staff of a multiuser facility is significant.

The importance of understanding any XPS data from analysis of the whole data set, including survey spectra, should not be overlooked, especially as this can readily show the presence of contaminants or the formation of a particular species (e.g., surface carbonates). Complementary to what should be standard protocols for data analysis, to further facilitate understanding, we believe that training users to appreciate studying controlled changes in data sets, whilst potentially instrumentally intensive, can save significant time in data analysis and enhance both the understanding and experience of users in respect of data analysis, especially in the selection of suitable peak shapes for fitting. This insight note is aimed at both new and experienced practitioners with a view to enable researchers to look for, understand and use to their advantage controlled changes in photoelectron spectra.

2 | Methods for Obtaining Peak Shapes

Obtaining reliable peak shapes for fitting is critical in spectral interpretation. Whilst the fundamental and theoretical peak shape for photoemission peaks is Lorentzian, this is usually convoluted with some Gaussian form, which can generally be modelled using Voigt or pseudo-Voigt functions [2, 3]. However, peak shapes are not always Voigt-like and complexity can be introduced through asymmetry [4–6], shake-up satellites [7], plasmons [8, 9] and multiplet splitting [10]. Below, we highlight methods for obtaining suitable peak shapes for analysis, together with any correlated satellite structure.

It is noted at this point that for insulating samples, the need for a stable charge balance at the surface is essential to avoid spectral artefacts.

2.1 | Bulk Material and Standards

Collection of spectra from standard reference materials is an excellent way of obtaining core-level spectra and is especially useful for metals, which can be etched clean in situ prior to analysis. Figure 1 shows an example of the use of fitted spectra, derived from bulk metallic and oxide samples to fit the relatively complex Au(4d)/Pd(3d) spectral region for a AuPd bimetallic catalyst. As the spectra are collected under identical system settings, these standard spectra give insights into peak FWHMs and any extra structure, which should be included in any fit.

A potential downside to the collection of standard spectra is the history of the handling of the sample. Transition metal oxides, which have previously been opened, may react with the atmosphere forming surface carbonates and hydroxides [11–17]. In such cases, whilst bulk sensitive techniques such as XRD or Raman may indicate a high purity material, the surface is ultimately not representative of the bulk chemistry, and any derived line shape should be treated with some caution. It is recommended that samples are opened and introduced to the spectrometer by means of a glove box or appropriate vacuum transfer vessel [18–20]. In situ heat treatment, to remove adsorbed species, may also be useful.

2.2 | Angle-Resolved XPS (ARXPS)

Angular data can be used to extract line shapes, using methods we will discuss in Section 2.3. Figure 2a shows the angular data (normal emission (0 °) up to grazing emission (60°)) for a partially oxidised Ti-containing alloy, together with two peak shapes extracted from the data. Whilst Shape 1 is reminiscent of metallic Ti (BE $2p_{3/2} = 454.0$ eV), Shape 2 has features and energies consistent with TiO_2 (BE $2p_{3/2} = 458.6$ eV) but also reveals at least one state correlated with the TiO_2, likely a Ti (II)-oxide based on the binding energy (BE $2p_{3/2} = 455.5$ eV).

Whilst the presence of TiO_2 is clear, the presence of a suboxide may be overlooked, despite being inferred by the increased asymmetry of the metallic Ti signal with increasing angle. Key in this data processing is not only the identification of the second oxide but also its positioning relative to the other Ti states, which can aid curve-fitting and yield a greater understanding of the surface chemistry.

2.3 | Controlled Oxidation and Reduction (REDOX)

The changes imparted on photoelectron spectra by, for example, oxidation, can yield valuable information in the derivation of peak shapes for detailed chemical state analysis where multiple oxidation states exist, as already noted for ARXPS data [21].

Controlled oxidation of polycrystalline and single crystal materials has long been a mainstay in surface science [22]. Oxidation has been achieved using dioxygen [22, 23] and nitrogen oxides [21, 24, 25], whilst more atomic-like oxygen sources such as O_3 [26–28] and plasmas [29–33] can readily yield thicker oxide layers. Such oxidation methods are excellent as the user can generate spectra free of adventitious carbon contamination or

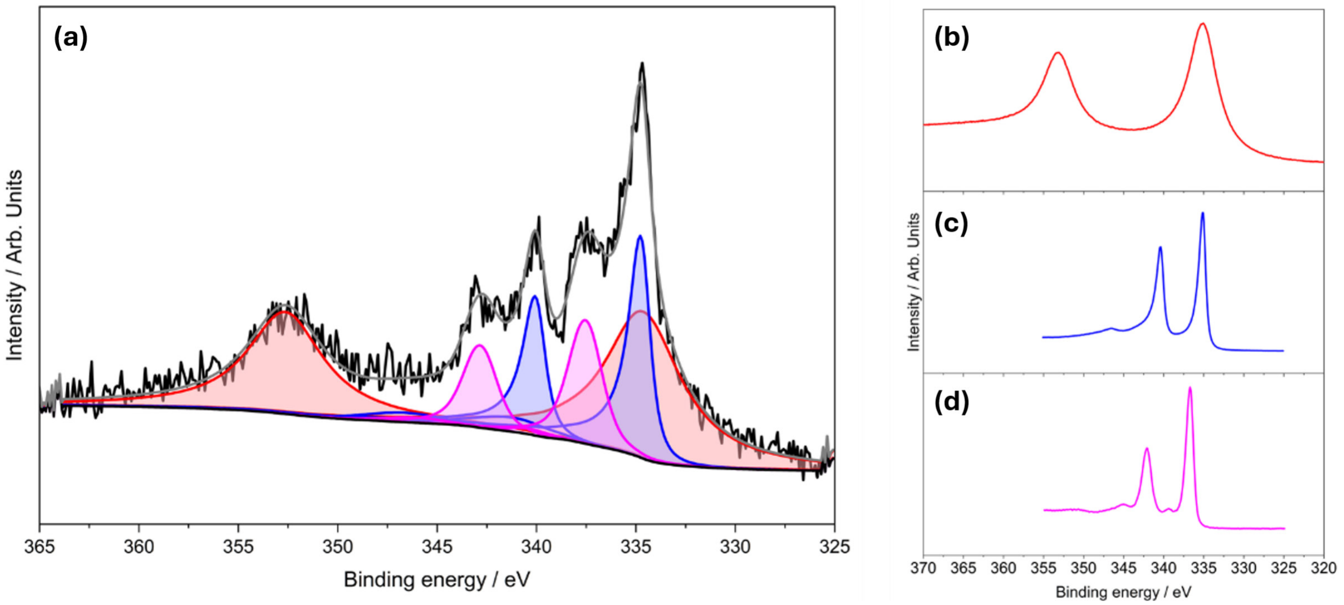

FIGURE 1 | Use of spectral shapes taken from bulk standards to fit a complex spectrum. Where (a) fitted spectrum using fits derived from fits (not shown) for metallic Au and Pd spectra (b) and (c), respectively, and (d) bulk PdO.

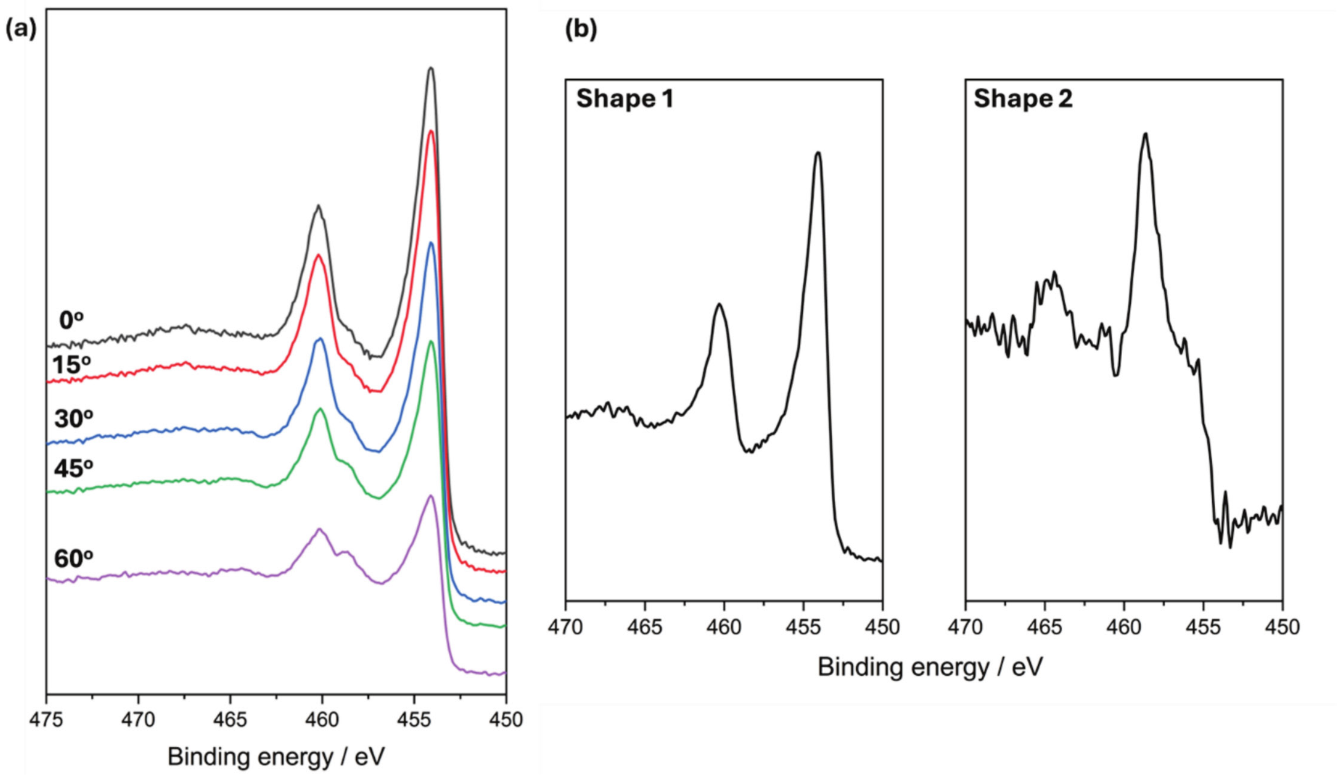

FIGURE 2 | (a) Ti(2p) ARXPS data between 0 (normal emission) and 60° (grazing emission) used to generate Shapes 1 and 2 as shown in (b). The two shapes have been obtained using PCA and algebraic methods as previously discussed.

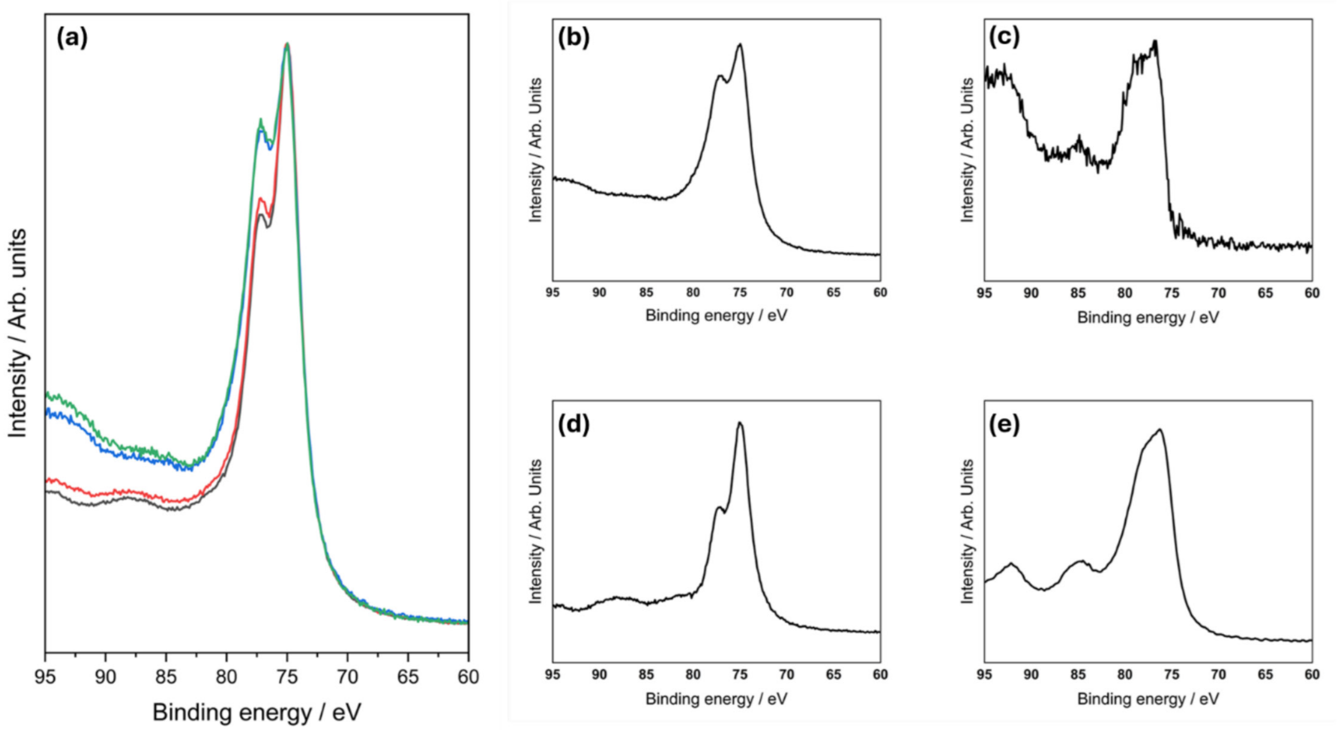

FIGURE 3 | Cu(3p) spectra for oxidation of a Cu_2O single crystal, where (a) normalised overlay of selected spectra from the oxidation sequence, (b) the final oxidised spectrum, (c) and (d) Cu(II) and Cu(I) peak shapes derived from the oxidation sequence and (e) is a reference bulk CuO spectrum—note the similarities to (c), with only the background changing.

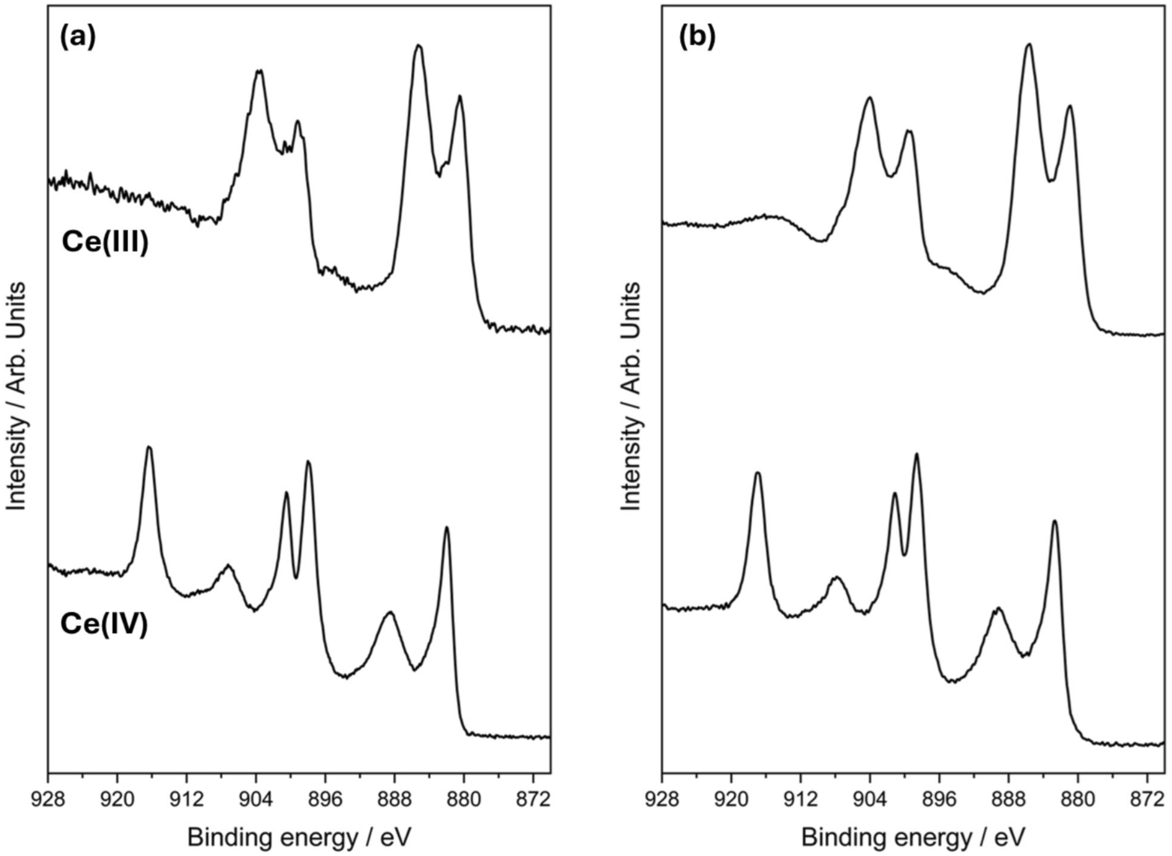

FIGURE 4 | Ce(3d) core-level spectra of (a) Ce(IV) and Ce(III) PCA enhanced states extracted from spectra acquired during the photoreduction of CeO_2, and (b) the equivalent bulk reference oxide spectra.

surface hydroxyls; furthermore, they allow the experimentalist to follow changes in core and Auger peaks as a function of oxidation, which can aid chemical state determination, such as that required for Cu or Zn [23, 34, 35]. Oxidation using O_3 can be achieved through the addition of a Hg-vapour lamp to the load-lock or ancillary chamber of a spectrometer [36]. Oxidation can also occur through the adsorption of residual chamber gases for highly reactive metals such as lanthanides [37]. Following changes can be made through careful spectral subtraction [21] or using principal component analysis (PCA) and algebraic methods [38, 39]; an example of this method for the oxidation of a Cu_2O single crystal is given in Figure 3.

Similarly, reduction can be performed using a ‘hydrogen cracker’ to obtain atomic hydrogen [40–42], or a reaction or gas treatment cell (sometimes referred to as a catalysis cell) generally with, for safety and gas pumping efficiency, diluted H_2 feeds [20, 43].

Series of spectra collected from controlled reduction through x-rays [44, 45] or ions [46, 47] can extract practical line shapes representative of pure or intermediate chemical states for metal oxides and polymer or organic materials [48, 49]. As shown in Figure 4, it is possible to extract representative Ce(IV) and Ce(III) oxide spectra from the controlled reduction of CeO_2 [44]; similar methods have been used to obtain distinct Mo line shapes [39]. Where reduced (or oxidised) species may have different levels of conductivity, such as in the case of molybdenum oxides (MoO_3 is an insulator, whilst MoO_2 is conductive), then mounting such samples, so they are floated from the spectrometer will aid in a more uniform charge balance across the surface.

3 | Summary

We have highlighted that performing experiments in such ways that impart changes in the photoelectron spectra allows a considerable deal of underlying chemistry to be extracted. Such changes yield spectra suitable for the derivation of line shapes for fitting or components for PCA and related analysis. We reiterate here that although peak shapes can be derived from manipulation of spectra, for a rigorous and informed analysis of any data, the whole data set should be analysed, including survey spectra. Importantly, readers of this insight note are encouraged to go read the given references and try the methods outlined therein with their own work.

Acknowledgements

The authors acknowledge the EPSRC who funds the provision of the EPSRC National Facility for Photoelectron Spectroscopy (‘HarwellXPS’, EP/Y023587/1, EP/Y023609/1, EP/Y023536/1, EP/Y023552/1 and EP/Y023544/1).

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request subject to the authors' institutes' guidelines.

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