ASTM D5946
ASTM D7334
ASTM D7490
ISO 27448

optical contact angle measurements and drop contour analysis to determine surface energy as well as interfacial and surface tension

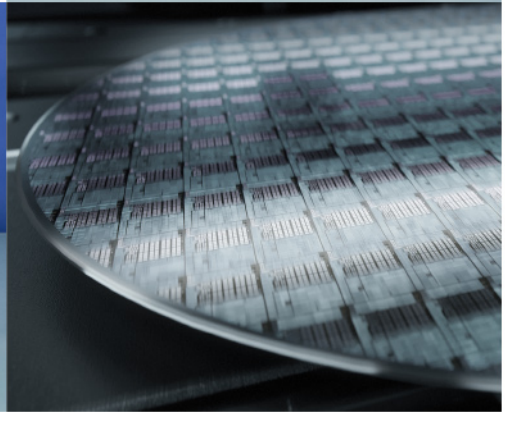
force tensiometry, dynamic contact angle measurements, and force of adhesion evaluation

ASTM D1331
ASTM D1417
ISO 1409

ISO/TR 13097

optical turbidity, stability and aging analysis of multi-phase dispersions

zeta potential measurements of fibres, powders, and plate-shaped solids



High-end, versatile laboratory measurement device portfolio for a comprehensive analysis of surfaces and interfaces

Learn more >

dataphysics
Understanding Interfaces

DataPhysics Instruments GmbH
Raiffeisenstraße 34 • 70794 Filderstadt, Germany
phone +49 (0)711 770556-0 • fax +49 (0)711 770556-99
sales@dataphysics-instruments.com
www.dataphysics-instruments.com

Check for updates

Received: 13 October 2022 | Revised: 6 February 2023 | Accepted: 7 February 2023

DOI: 10.1002/sia.7205

NOTES AND INSIGHTS

SURFACE and INTERFACE ANALYSIS WILEY

XPS insights: Sample degradation in X-ray photoelectron spectroscopy

David J. Morgan [1,2,3]

[1]Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Cardiff, UK

[2]School of Chemistry, Cardiff University, Cardiff, UK

[3]HarwellXPS – The EPSRC National Facility for Photoelectron Spectroscopy, Research Campus at Harwell (RCaH), Didcot, UK

Correspondence
David J. Morgan, Cardiff Catalysis Institute, Translational Research Hub, Cardiff University, Maindy Road, Cardiff CF24 4HQ, UK.
Email: morgandj3@cardiff.ac.uk

Funding information
Engineering and Physical Sciences Research Council, Grant/Award Number: PR16195

Standard X-ray photoelectron spectroscopy (XPS) analysis is thought of by many as a non-destructive form of analysis; however, both the interaction of the X-ray photons and the subsequent electron cascade can cause significant changes to the analysed area. This *XPS Insights* paper gives a brief overview to this phenomenon, supported by specific examples and experimental advice to assess and minimise damage during analysis.

KEYWORDS
damage, degradation, insight, XPS

1 | INTRODUCTION: CAUSES AND SOURCES OF DAMAGE

Damage typically occurs from the interaction of primary or secondary radiation sources, such as photons and electrons, with a sample. The damage may not be limited to the surface, with the effect of the damage propagating throughout the bulk of the material due to the penetration depth of the X-ray photon and the subsequent cascade of high-energy photoelectrons and thermalisation processes. Figure 1 shows a simple representation of some of the damage that may occur; a more exhaustive list can be found in Baer et al.[1]

The potential for damage in recorded spectra should not be ignored, and analysts should familiarise themselves with ISO Standard 18554:2016 - 'Surface chemical analysis — Electron spectroscopies — Procedures for identifying, estimating and correcting for unintended degradation by X-rays in a material undergoing analysis by X-ray photoelectron spectroscopy' for a simple procedure to estimate and correct for degradation. Note, however, the standard does not address comparisons between sample types and neither does it address degradation mechanisms.

In the flowing sections of this *XPS Insight*, a brief overview of sample damage for different sample types during XPS analysis is presented and strategies for minimisation of spectral artefacts from such damage.

1.1 | Polymers, organics and 'soft matter'

Polymers tend to undergo degradation through loss of volatile compounds such as HCl in the case of chlorinated polymers,[2–10] or through crosslinking of unsaturated functions or bond scission.[11,12] In contrast, phenyl-based polymers such as polystyrene and PET tend to be stable under X-ray analysis which is attributed to the delocalised electrons acting as a 'sponge' and absorbing excess energy.[2]

Beamson and Briggs introduced the polymer degradation index[2] as a measure of how different polymers/classes of polymer degrade over a period of 500 min by following the change in the X/C ratio, where X is typically a parameter characteristic of the polymer obtainable from the photoelectron spectrum, such as the area of Cl, F, O and so forth. This index, whilst useful in understanding degradation rates, is limited in that modern spectrometers, especially those with micro-focussed sources, have a significant impact on the rate of degradation. This effect has been shown by the current

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.
© 2023 The Author. *Surface and Interface Analysis* published by John Wiley & Sons Ltd.

10969918, 0, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/sia.7205 by Cardiff University, Wiley Online Library on [02/03/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

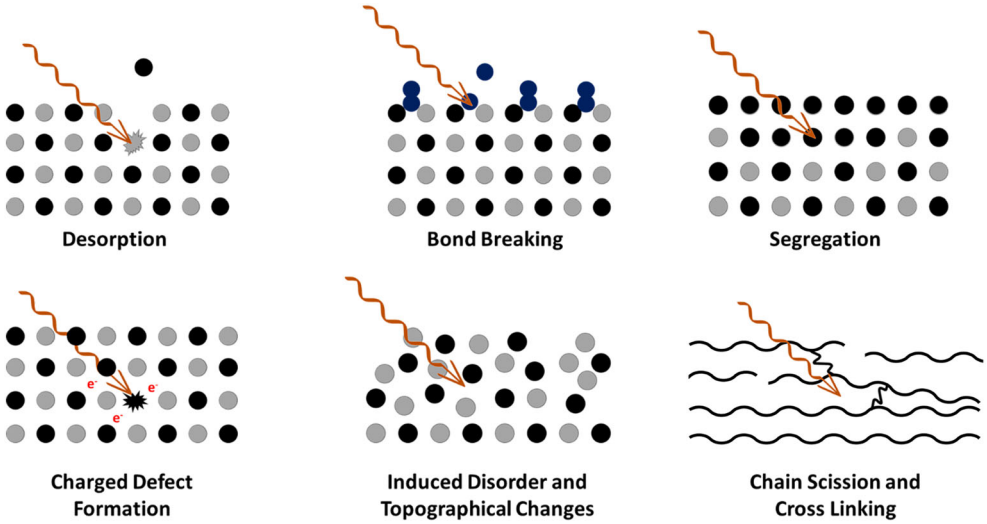


FIGURE 1 Types of damage that may occur from the interaction of the incoming X-ray photon and generated electron cascade in a material during X-ray photoelectron spectroscopy (XPS) analysis. Adapted from Baer et al.[1]

author, with the degradation rate for one micro-focussed XPS system doubling with a halving of the spot size, in agreement with that of Cazaux.[13–15]

Such degradation can readily be seen in polyvinyl chloride (PVC), which is typically used as the exemplar for polymer degradation as it undergoes rapid dechlorination forming a network of polyenes. Figure 2 shows the change in Cl/C ratio for PVC as measured on two different monochromatic XPS systems and clearly illustrates the marked difference between a micro-focussed XPS system and that of varying spot size. Clearly, the shape of the plots between the two systems is very different, with the broad spot source having a linear profile, whilst the other has a more exponential decay, the linear region being confined to approximately the first 30 min.

Given the increased use of micro-focussed XPS systems, the Beamson and Briggs degradation index is perhaps somewhat dated, given the long degradation times specified and the specific instrument. Instead, a Photon Threshold Index (PTI) for a system is recommended whereby all polymers are scaled relative to the reduction of PVC measured on that particular instrument.[15,16]

Nevertheless, irrespective of the system, given the propensity for degradation, rapid acquisition of the significant core levels for polymeric materials is preferrable to minimise spectral artefacts.

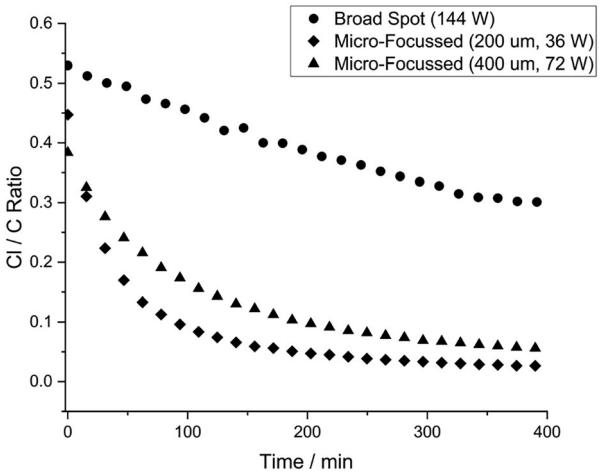


FIGURE 2 Plot of Cl/C ratio against time for physical vapor deposition (PVD) degradation on two different X-ray photoelectron spectroscopy (XPS) systems. Also shown is the data for a smaller spot size on the micro-focussed XPS system (data adapted from Morgan and Uthayasekaran[15]).

1.2 | Inorganic materials: Metal oxides, salts, ionic lattices and supported nanoparticles

Inorganic materials are typically considered stable during XPS analysis; however, there are numerous examples of analysis-induced damage. It is logical to assume those which are non-conducting (the majority of materials) and those with weak bonds may be especially susceptible to reduction, as discussed by Cazaux.[14]

Süzer has shown the reduction of different metal ions deposited on Au and Si wafers and related their reducibility to the electrochemical reduction potential of the metal ion,[17] whilst Auger decay mechanisms, Coulomb explosion or decomposition of ligands via photoreduction have all been identified as decomposition routes.[18]

Irrespective of the decay mechanism, which is outside the scope of this insight note, the possibility that a sample may be susceptible to reduction during analysis should always be assumed. Figure 3 shows just some of the samples that can undergo reduction as measured on different XPS systems in the author's laboratory. A non-exhaustive list of other metal oxides and salts which have been reported to degrade under analysis include Au,[19] Pd,[20] Cu,[21–23] Re,[24] V,[22,25–27] Cr,[22] Ti,[28,29] Pb,[30,31] Mo,[20,32,33] W,[17] U,[34] Ce[35,36] and Te [this work].

It is logical to assume also that rates of reduction may be different for nanoparticulate materials given their size and surface-to-volume ratio strongly affecting their surface properties and overlayer thicknesses.[37,38]

10969918, 0, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/sia.7205 by Cardiff University, Wiley Online Library on [02/03/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

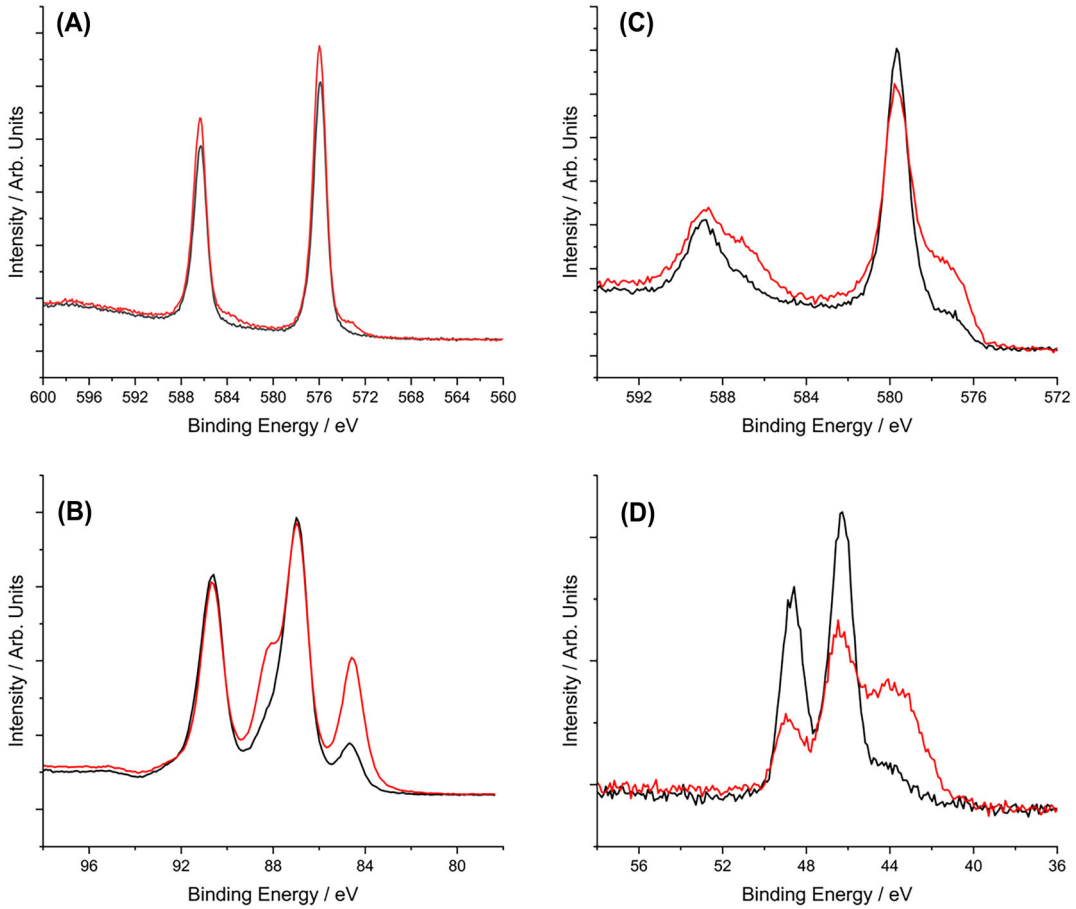


FIGURE 3 Examples of analysis-induced damage, recorded on different X-ray photoelectron spectroscopy (XPS) systems in the author's laboratory, where: (A) Te (3d) core-level for tellurium dioxide (TeO_2), (B) Au (4f) core-level for an Au/C catalyst used for acetylene hydrochlorination, (C) Cr (2p) core-level for a chromium (VI) oxide (CrO_3) flake and (D) Re (4f) core-level for a supported Re/ZnO catalyst. Black = core-level recorded first for the received sample, red = core-level recorded at the end of the analysis.

1.3 | Thin films and self-assembled monolayers

Insulating thin film and related materials can be extremely susceptible to analysis-induced damage. Such damage arises from the electrons generated from the substrate being injected into the film overlayer, as discussed theoretically by Cazaux.[39] Such an effect has been demonstrated for PVA films on Si, Cu and Au substrates, with greater damage observed for the metallic substrates, which were correlated with photoelectron yield and substrate secondary electron emission[40]; similar dependencies for SAMs on Si and Au substrates have been noted by Laibinis et al.[41] Again, in such analysis, the role of both X-ray and neutralising sources should be considered for possible enhancement of damage in addition to electron injection from the substrate.

2 | INSTRUMENTAL EFFECTS AND MINIMISING DAMAGE

Given the potentially damaging nature of XPS analysis, how do we minimise such damage?

First, it is important to note that all XPS systems operate differently and that the operating parameters will also vary and affect the quality of the data recorded. Therefore, it is beneficial for the system operator to understand factors that influence reduction, which can be broadly broken down in to (i) instrumental factors which the analyst has at least some control (e.g., X-ray power and sample mounting) or no control over (e.g., sample type and source type) and (ii) sample dependent factors which are touched upon below.

1. Instrumental factors:
    1. X-ray power and type of illumination (broad spot or micro-focussed)
    2. X-ray source (monochromatic vs. non-monochromatic)
    3. Charge compensation source (electron or electron and argon ion)
    4. Ability to cool samples (cooling can minimise damage)
    5. Length of time in vacuum (residual chamber gases can change a surface)
2. Sample dependent factors:
    1. Electrical and thermal properties (can aid dissipation of damage)

10969918, 0, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/sia.7205 by Cardiff University, Wiley Online Library on [02/03/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

2. Surface contamination and sample history (previous analysis or presence of surface contamination may show enhanced reduction)
3. Bulk or thin film material (see section on thin films)
4. Method of mounting (can the sample be cooled as mounted?)

To minimise damage, we should start with the view that the sample to analyse will degrade in some way and adjust our analysis methodology to mitigate artefacts in our spectra. The analyst should first ask the following questions:

1. Are there reducible metal states in the sample/is the sample polymeric?
2. Have they observed sensitivity of similar samples to the charge compensation source?
3. Have they observed increased reduction from micro-focussed X-rays?

Answers to such questions may preclude the use of a particular XPS system or, more likely, allow for adjustment of experimental procedures. For example, should we have an elemental state, such as Cu (II), which is known to reduce, the experimental procedure should be adapted so that it is collected as the first and last regions to check levels of reduction. Alternatively, the Cu (2p) region could be collected as a series of single scans, so each spectrum can be retrospectively checked for damage and the 'undamaged' spectra summed for quantification purposes.

The approach the analyst uses will be both sample and system dependent, but sometimes there is no escape from collecting data over shorter time frames and accepting a lower signal-to-noise ratio in the spectrum or collecting at higher pass energies (e.g., 40 eV rather than 20 eV) to increase the count rate.

Irrespective of these points, overall minimisation of X-ray exposure during analysis is preferrable. As a case in point, during the operation of the EPSRC national facility for photoelectron spectroscopy, we often have users new to surface analysis and regularly give some form of introduction to the technique, usually with samples in the system. Of course, the use of the visitors' samples for this discussion could lead to significant sample damage as the sample is continuously irradiated. Therefore, we tend to use what we consider to be stable, sacrificial samples, such as TiO_2, Kapton or PET, depending on the users' samples, as exemplars to aid discussion.

3 | SUMMARY

This *XPS Insight* has sought to give a brief oversight on sample degradation during XPS analysis. Whilst usually considered in the analysis of polymers, it is often overlooked for inorganic materials leading to misleading or erroneous conclusions from XPS data. It is hoped that analysts will adopt and use the data and strategies presented herein to understand their own spectrometer and ultimately yield spectra with minimal artefacts, hence representative of the samples studied.

ACKNOWLEDGEMENTS

Some of the data collected in this work was acquired at the Engineering and Physical Sciences Research Council (EPSRC) National Facility for XPS ("HarwellXPS"), operated by Cardiff University and UCL, under EPSRC contract no. PR16195

DATA AVAILABILITY STATEMENT

Data sharing not applicable to this article as no datasets were generated or analysed during the current study.

ORCID

David J. Morgan https://orcid.org/0000-0002-6571-5731

REFERENCES

1. Baer DR, Gasper DJ, Engelhard MH, Lea SA. Beam effects during AES and XPS analysis. In: Briggs D, Grant J, eds. *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*. Manchester: IM Publications; 2003.
2. Beamson G, Briggs D. *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*. Wiley-Blackwell; 1992.
3. Artyushkova K, Fulghum JE. Quantification of PVC-PMMA polymer blend compositions by XPS in the presence of x-ray degradation effects. *Surf Interface Anal*. 2001;31(5):352-361. doi:10.1002/sia.953
4. Chang HP, Thomas JH. An XPS study of X-ray-induced dehydrochlorination of oxygen-free PVC. *J Electron Spectros Relat Phenomena*. 1982;26(3):203-212. doi:10.1016/0368-2048(82)85028-7
5. Manfredini M, Atzei D, Elsener B, Marchetti A, Rossi A. Degradation of plasticized PVC for biomedical disposable device under soft x-ray irradiation. *Surf Interface Anal*. 2003;35(3):294-300. doi:10.1002/sia.1532
6. Engelhard M, Baer D, Lea S. Beam damage of poly(2-chloroethyl methylacrylate) [PCEMA] films as observed by X-ray photoelectron spectroscopy at 143 K, 303 K, and 373 K. *Surface Science Spectra*. 2003;10(1):80-100. doi:10.1116/11.20030902
7. Yoshihara K, Tanaka A. Interlaboratory study on the degradation of poly (vinyl chloride), nitrocellulose and poly (tetrafluoroethylene) by x-rays in XPS. *Surf Interface Anal*. 2002;33(3):252-258. doi:10.1002/sia.1208
8. Seah MP, Spencer SJ. Degradation of poly (vinyl chloride) and nitrocellulose in XPS. *Surf Interface Anal*. 2003;35(11):906-913. doi:10.1002/sia.1618
9. Militello MC, Gaarenstroom SW. X-ray beam damage of poly (vinyl chloride) (PVC). *Surface Science Spectra*. 2003;10(1):127-136. doi:10.1116/11.20030804
10. Engelhard M, Krishna A, Kulkarni P, Lee C-Y, Baer D. Beam damage of poly (vinyl chloride) [PVC] film as observed by X-ray photoelectron spectroscopy. *Surface Science Spectra*. 2003;10(1):57-66. doi:10.1116/11.20040601
11. Cumpson PJ, Portoles JF, Sano N, Barlow AJ. X-ray enhanced sputter rates in argon cluster ion sputter-depth profiling of polymers. *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*. 2013;31(2):021208. doi:10.1116/1.4793284
12. Charlesby A. Crosslinking and degradation of polymers. *Radiation Physics and Chemistry (1977)*. 1981;18(1–2):59-66. doi:10.1016/0146-5724(81)90064-9
13. Cazaux J. Prospects in high resolution X-ray photoelectron microscopy. *Ultramicroscopy*. 1985;17(1):43-49. doi:10.1016/0304-3991(85)90175-5
14. Cazaux J. The influence of radiation damage (microscopic causes) on the sensitivity of Auger electron spectroscopy and X-ray

10969918, 0, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/sia.7205 by Cardiff University, Wiley Online Library on [02/03/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

photoelectron spectroscopy. *Applications of Surface Science*. 1985; 20(4):457-471. doi:10.1016/0378-5963(85)90167-9
15. Morgan DJ, Uthayasekaran S. Revisiting degradation in the XPS analysis of polymers. *Surf Interface Anal*. 2022. doi:10.1002/sia.7151
16. Baer DR, Engelhard MH, Lea AS, Saraf LV. Simple method for estimating and comparing x-ray damage rates. *J Vac Sci Technol a*. 2005; 23(6):1740-1744. doi:10.1116/1.2073387
17. Süzer Ş. XPS investigation of X-ray-induced reduction of metal ions. *Appl Spectrosc*. 2000;54(11):1716-1718. doi:10.1366/0003702001948772
18. Thomas JH III. Photon beam damage and charging at solid surfaces. In: Czanderna AW, Madey TE, Powell CJ, eds. *Beam Effects, Surface Topography and Depth Profiling in Surface Analysis*. New York: Kluwer Academic Publishers; 2002:1-37.
19. Fong Y-Y, Visser BR, Gascooke JR, et al. Photoreduction kinetics of sodium tetrachloroaurate under synchrotron soft X-ray exposure. *Langmuir*. 2011;27(13):8099-8104. doi:10.1021/la200463k
20. Fleisch TH, Zajac GW, Schreiner JO, Mains GJ. An XPS study of the UV photoreduction of transition and noble metal oxides. *Appl Surf Sci*. 1986;26(4):488-497. doi:10.1016/0169-4332(86)90120-0
21. Biesinger MC, Lau LWM, Gerson AR, Smart RSC. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn. *Appl Surf Sci*. 2010;257(3):887-898. doi:10.1016/j.apsusc.2010.07.086
22. Edwards L, Mack P, Morgan DJ. Recent advances in dual mode charge compensation for XPS analysis. *Surf Interface Anal*. 2019;51(9):925-933. doi:10.1002/sia.6680
23. di Castro V, Piredda G. Photoinduced reduction of silica supported CuO during XPS irradiation. *Chem Phys Lett*. 1985;114(1):109-113. doi:10.1016/0009-2614(85)85065-X
24. Iqbal S, Shozi ML, Morgan DJ. X-ray induced reduction of rhenium salts and supported oxide catalysts. *Surf Interface Anal*. 2017;49(3): 223-226. doi:10.1002/sia.6076
25. Knotek ML, Feibelman PJ. Stability of ionically bonded surfaces in ionizing environments. *Surf Sci*. 1979;90(1):78-90. doi:10.1016/0039-6028(79)90011-6
26. Zabilska A, Clark AH, Ferri D, Nachtegaal M, Kröcher O, Safonova OV. Beware of beam damage under reaction conditions: X-ray induced photochemical reduction of supported VO_x catalysts during *in situ* XAS experiments. *Phys Chem Chem Phys*. 2022;24(36): 21916-21926. doi:10.1039/D2CP02721F
27. Chenakin SP, Prada Silvy R, Kruse N. Effect of X-rays on the surface chemical state of Al_2O_3, V_2O_5, and aluminovanadate oxide. *J Phys Chem B*. 2005;109(30):14611-14618. doi:10.1021/jp051944j
28. Chang SH, Kim J, Phatak C, et al. X-ray irradiation induced reversible resistance change in Pt/TiO_2/Pt cells. *ACS Nano*. 2014;8(2):1584-1589. doi:10.1021/nn405867p
29. Kruse N, Chenakin S. XPS characterization of au/TiO_2 catalysts: binding energy assessment and irradiation effects. *Appl Catal Gen*. 2011; 391(1-2):367-376. doi:10.1016/j.apcata.2010.05.039
30. McGettrick JD, Hooper K, Pockett A, et al. Sources of Pb(0) artefacts during XPS analysis of lead halide perovskites. *Mater Lett*. 2019;251: 98-101. doi:10.1016/j.matlet.2019.04.081
31. Li Y, Xu X, Wang C, et al. Light-induced degradation of $CH_3NH_3PbI_3$ hybrid perovskite thin film. *J Phys Chem C*. 2017;121(7):3904-3910. doi:10.1021/acs.jpcc.6b11853
32. Baltrusaitis J, Mendoza-Sanchez B, Fernandez V, et al. Generalized molybdenum oxide surface chemical state XPS determination via informed amorphous sample model. *Appl Surf Sci*. 326:151-161. doi:10.1016/j.apsusc.2014.11.077
33. Garland BM, Fairley N, Strandwitz NC, Thorpe R, Bargiela P, Baltrusaitis J. A study of in situ reduction of MoO_3 to MoO_2 by X-ray photoelectron spectroscopy. *Appl Surf Sci*. 2022;598:153827. doi:10.1016/j.apsusc.2022.153827
34. Qiang S, Wang J, Wang Y, et al. Analysis of the uranium chemical state by XPS: is what you see real? *Appl Surf Sci*. 2022;576:151886. doi:10.1016/j.apsusc.2021.151886
35. Paparazzo E, Ingo GM, Zacchetti N. X-ray induced reduction effects at CeO_2 surfaces: an x-ray photoelectron spectroscopy study. *J Vac Sci Technol a*. 1991;9(3):1416-1420. doi:10.1116/1.577638
36. Paparazzo E. XPS studies of damage induced by X-ray irradiation on CeO2 surfaces. *Surf Sci*. 1990;234(1–2):L253-L258. doi:10.1016/0039-6028(90)90658-U
37. Karakoti AS, Hench LL, Seal S. The potential toxicity of nanomaterials—the role of surfaces. *JOM*. 2006;58(7):77-82. doi:10.1007/s11837-006-0147-0
38. Baer DR. The chameleon effect: characterization challenges due to the variability of nanoparticles and their surfaces. *Front Chem*. 2018; 6:145. doi:10.3389/fchem.2018.00145
39. Cazaux J. About the charge compensation of insulating samples in XPS. *J Electron Spectros Relat Phenomena*. 2000;113(1):15-33. doi:10.1016/S0368-2048(00)00190-0
40. Beamson G, Briggs D. Degradation of poly (vinyl alcohol) thin films during monochromatized XPS: substrate effects and x-ray intensity dependence. *Surf Interface Anal*. 1998;26(5):343-351. doi:10.1002/(SICI)1096-9918(19980501)26:5003C343::AID-SIA377003E3.0.CO;2-M
41. Laibinis PE, Graham RL, Biebuyck HA, Whitesides GM. (1991) X-ray damage to CF_3 CO_2-terminated organic monolayers on Si/Au: principal effect of electrons. *Science*. 1979;254(5034):981-983.

How to cite this article: Morgan DJ. XPS insights: Sample degradation in X-ray photoelectron spectroscopy. *Surf Interface Anal*. 2023;1-5. doi:10.1002/sia.7205

10969918, 0, Downloaded from https://analyticalsciencejournals.onlinelibrary.wiley.com/doi/10.1002/sia.7205 by Cardiff University, Wiley Online Library on [02/03/2023]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License