

X-ray induced reduction of a surfactant/polyoxotungstate hybrid compound

Aaron V. Colusso, Andrew McDonagh, Michael B. Cortie*

Institute for Nanoscale Technology, School of Mathematical and Physical Sciences, University of Technology Sydney, Ultimo NSW 2007, Australia

Email: michael.cortie@uts.edu.au

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Abstract

We investigate the spontaneous reduction of a photochromic surfactant/polyoxotungstate hybrid during repeated XPS scans and show how this effect may confound attempts to use soft X-rays to characterize materials of this nature. The W4f core-level spectra revealed a progressive increase of W⁵⁺ and W⁴⁺ species at the expense of W⁶⁺ as irradiation time increased. The samples developed a blue color attributed to the presence of W⁴⁺ and/or W⁵⁺. The progressive photoreduction is also associated with a shift of the W⁶⁺ peak within the W4f spectrum to lower binding-energies. This work highlights the need to consider inadvertent changes in oxidation state during XPS characterization of samples containing photoreducible transition metals.

Introduction

The proliferation of techniques such as X-ray photoelectron spectroscopy (XPS), small angle X-ray scattering (SAXS), X-ray adsorption spectroscopy (XAS) and X-ray diffraction (XRD) has contributed greatly to modern science. X-rays have sufficient energy to instigate the ionization of atoms¹⁻⁴ and such events can create highly reactive free-radicals in molecules. Secondary and Auger electron cascades can reduce or oxidize neighbouring atoms and cause further ionization events.⁵⁻⁷ These events have the potential to drastically alter the chemical, and therefore structural, composition of a material.^{6,8} X-ray induced damage is often encountered and quite familiar in the biological sciences, especially in the field of protein crystallography^{1,9} where the determination of complex protein crystal structures utilizes spectroscopic techniques such as XAS and SAXS that employ high-energy, short wavelength X-rays. However, its occurrence in materials science is often overlooked.

Chemical changes induced by X-ray interactions can occur in some metal oxides.^{3,5,10-16} Photoionization of oxo-ligands results in ejected hot-electrons relaxing onto metal cations. The Auger cascades that usually result from these photoionization events can progressively ionize oxo-ligands to yield cationic oxygen species; $O^{2-} \rightarrow 3e^- + O^+$. These oxygen cations may be ejected from the lattice (Coulombic explosion) due to the repulsion with neighbouring metallic cations^{3,5,17} leading to the creation of oxygen-vacancies and hence, substoichiometry.^{7, 20} Metal cations with no valence electrons (e.g., Cr^{6+} , Fe^{3+} , Cu^{2+} and Ce^{4+}) are highly susceptible to X-ray induced photoreduction.^{3-5,14-16,18} X-rays can also break bonds between adsorbed H_2O and O_2 , forming reactive monoatomic ions that can react with the surface.^{10-12,19}

The presence of organic molecules, within a material or surface contamination, accelerates X-ray-induced metal cation photoreduction. Photoionization and thermal-degradation of organic molecules creates reactive, reducing species, whilst the process of 'Coulombic explosion' is accelerated in metal-oxides due to the reaction between positively charged oxygen cations and oxidizable organic species leading to volatile oxygenated carbonaceous products.^{3,5,17}

XPS is a useful technique to determine the oxidation states of metal cations. For example, the measurement of the $M^{n+}/M^{(n-1)+}$ ratio (where $M = W, Mo$ or V) post UV photoreduction in group V and VI metal-oxide based photochromic²⁰⁻²³ and photocatalytic^{24,25} materials provides a means to determine the extent of the reaction. Unfortunately, XPS-derived determination of this ratio may return inaccurate results, due to additional photoreduction by the X-rays.^{20,21,23,26} To our knowledge no quantitative investigation has been reported examining these processes in group V and VI transition-metal-oxide inorganic-organic hybrid materials.

Here we present kinetic data describing the photoreduction of a photochromic, metal-oxide based inorganic-organic hybrid $(C_{19}H_{42}N)_7Cl[H_2W_{12}O_{42}] \cdot 2H_2O$ during XPS experiments.

Experimental

The synthesis of $(C_{19}H_{42}N)_7Cl[H_2W_{12}O_{42}] \cdot 2H_2O$ (designated in this work as CTA- W_{12}) has been described elsewhere²⁷. XPS measurements were conducted using a Thermo Scientific ESCALAB250Xi, utilizing monochromated Al K- α (1486.68 keV) radiation at a power of 120 W (13.8 kV \times 8.7 mA). The sample was pressed into a pellet on an Al stub which was then mounted on the instrument and electrically grounded. Charge-compensation techniques such as in-lens low-energy electrons and low-energy Ar^+ ion-flooding were not applied. A C(1s) binding-energy reference of 284.8 eV for adventitious hydrocarbon was used, with the spectrometer calibrated using Au(4f), Ag(3d₅) and Cu(2p₃) lines measured at 83.96, 368.21 and 932.62 eV respectively. Scans were collected within the same spot size of 400 μm , at a pass energy of 20 eV, with each scan taking 21.1 seconds to collect. The effect of vacuum alone was tested by holding the samples for 5 h in a vacuum of 3.9×10^{-4} Pa (2.9×10^{-6} torr), after which the samples were visually examined for any evidence of reduction (which would be indicated by a blue color).

Data were analysed with Fityk v.0.8.9²⁸ with the separation between W 4f_{7/2} and W 4f_{5/2} doublets fixed at 2.2 eV, and the ratio between their areas and full-width-half-maximum (FWHM) set at 4:3 and 1:1, respectively. A sensitivity factor of 6.181 was used to analyse W4f spectra, with the sensitivity factor of C 1s set to 1. Gaussian functions were fitted to the peaks using the Nelder-Mead Simplex after performing a Shirley-type

background subtraction. The $W5p_{3/2}$ satellite peak was not considered within the fitting parameters due to its non-contribution to the $W4f$ spectrum, and hence lack of influence on the determination of tungsten oxidation states.

Results

CTA- W_{12} is a photochromic surfactant-polyoxometalate hybrid consisting of layers of pseudo-hexagonally arranged polyoxometalate (POM) anions and water which is separated by the hydrophobic alkyl-tails of the cetyltrimethylammonium (CTA^+) cations.²⁷ Above band-gap (3.6 eV) radiation incident on the sample instigates an oxygen-to-metal ligand-to-metal charge-transfer ($O \rightarrow M$ LMCT), reducing W^{6+} to W^{5+} which results in the formation of a visible-light absorbing charge-transfer complex (Figure S1).^{20,22,23} It is therefore likely that soft X-ray irradiation (1.486 keV) will induce similar reduction of metallic cations.

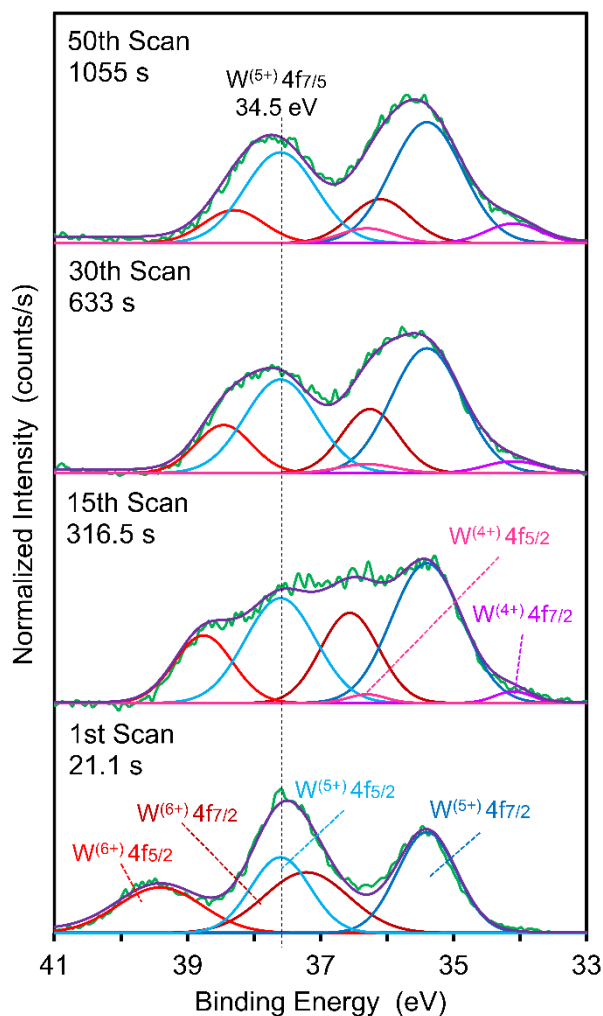


Figure 1. The first, fifteenth, thirtieth and fiftieth scans of the W4f core-level XPS spectra of CTA- W_{12}

The first, fifteenth, thirtieth and fiftieth scans of the W4f core-level XPS spectra of CTA- W_{12} are displayed in Figure 1. The sample had been subjected to several survey scans prior to the first displayed measurement. These survey scans had shown that carbon was present in two environments (most likely in the alkane chains, as well as bound to the cationic head group), and oxygen in two environments (the Keggin ion as well as in adsorbed H_2O).²⁹ $W4f_{5/2}$ and $W4f_{7/2}$ spin-orbit doublets of the W^{6+} and W^{5+} states appear at 39.4 and 37.2, and 37.6 and 35.4 eV, respectively. $W4f_{5/2}$ and $W4f_{7/2}$ spin-orbit doublets of the W^{4+} state, apparent within the fifteenth, thirtieth and fiftieth scans, appear at 36.3 and 34.1 eV. The reduction is accompanied by the development of a blue color in the sample. There was no change in the color of the sample if held in vacuum alone. This is the first report of W4f XPS of a metatungstate (i.e. a Keggin polyoxotungstate containing $2H^+$ as the ‘hetero-atom’). The binding-energies (BEs) reported here are somewhat different to that of analogous organic-polyoxometalate materials with, for example, the $W4f_{5/2}$ W^{6+} state being around 1.4 eV higher than the regularly reported 37.5-38.5 eV.^{23,26}

The relative proportions of the various tungsten oxidation states that contribute to the W4f core-level XPS spectra change significantly with successive XPS scans (Figure 1). The W^{6+} : W^{5+} ratio after the first scan was 46:54, indicating that there was already considerable reduction prior to this scan. The relative amount of

reduced W species increased with subsequent scans. After the fifth scan, significant amounts of W^{4+} were observed. After fifty scans, the $W^{6+}:W^{5+}:W^{4+}$ ratio was 21:70:9 indicating continued reduction of W by the X-ray beam.

The relative amounts of W^{6+} , W^{5+} and W^{4+} as a function of recorded irradiation time are displayed in Figure 2. The photoreduction of CTA- W_{12} occurred most rapidly during the first ~ 500 seconds (23 scans) and then slowed and reached saturation by ~ 900 seconds (42 scans). Similar photoreduction behaviour has been reported for the XPS-induced photoreduction of Cr^{6+} and U^{6+} compounds.^{3,14}

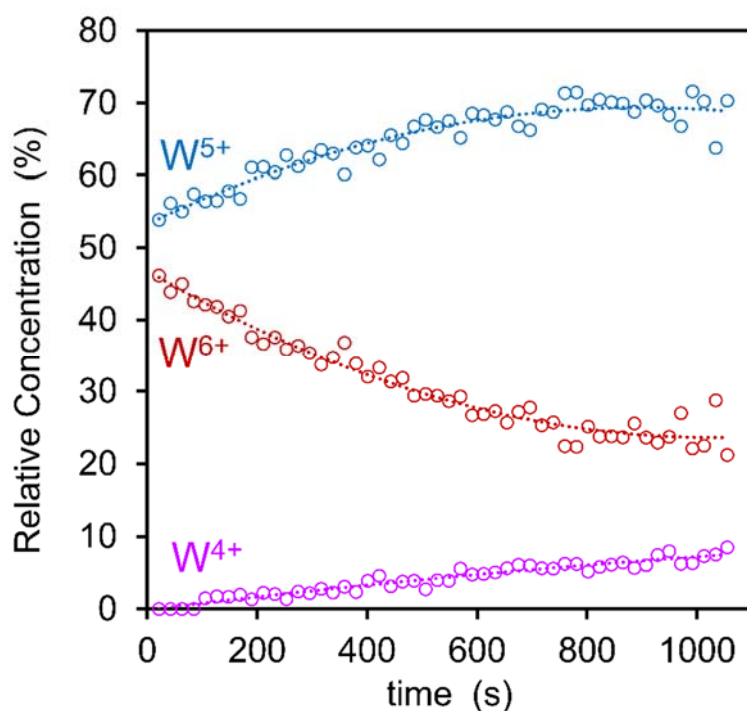


Figure 2. Relative concentration of W^{6+} , W^{5+} and W^{4+} oxidation states as a function of total scan time.

Figure S3 shows a 3D surface plot and a colour-map containing data from the $W4f$ spectra as a function of scan number. The trend towards the growth of reduced, lower oxidation states on the lower binding-energy side of the spectra at the expense of more oxidized, higher oxidation states on the higher binding-energy side is clearly visible. Three local maxima are apparent within the first 20 recorded spectra, corresponding to the sum of the $4f_{7/2}$ and $4f_{5/2}$ W^{6+} and W^{5+} doublets. During this time, the position (maximum intensity) of the peaks attributed to W^{6+} shift from 39.4 eV towards lower binding-energies (38.3 eV by the fiftieth scan). Xie *et al* observed similar behaviour of the W^{6+} oxidation state in their study of Ar^+ bombarded WO_3 .³⁰ In the present work, by the 25th scan, the W^{6+} doublets are largely enveloped by the increasingly prominent W^{5+} peaks, resulting in only two discernible local maxima in the $W4f$ spectra by this time. These two dominant local maxima persist until the end of the measurement, with the lower-binding energy peak slowly increasing in intensity and area during this time.

Discussion

These results suggest that the tungsten centres within the surfactant-POM organic-inorganic hybrid undergo a significant degree of reduction during XPS measurements. Since a UHV environment alone is not sufficient to cause loss of oxygen from the material, the reduction of the sample is attributed to the incidence of X-rays.

X-ray interaction with CTA- W_{12} would most likely occur at W-centres, considering the atomic number, Z , of W ($Z = 74$) is much higher than any other element present in the sample (Cl is the next highest

with $Z = 17$, then O with $Z = 8$). Since W present in CTA-W₁₂ is at its highest oxidation-state, W⁶⁺, it is highly likely that the processes of ‘Coulombic explosion’ is occurring with increasing scan/irradiation time.^{6,7,31,32} However, X-ray induced photoreduction of purely inorganic tungsten oxide samples, i.e. WO₃, is observed to be a slow process, attributed to the small, positive reduction potential of W⁶⁺ (+0.04 V vs hydrogen). For example, Suzer *et al* observed a small W⁵⁺ concentration increase after 80 hours of X-ray irradiation.¹³ Comparatively, W⁵⁺ and W⁴⁺ concentration within CTA-W₁₂ increases significantly within 1055 seconds (~18 min). Therefore, other X-ray induced photoreduction processes must also be occurring.

The X-ray absorbing W-centres in CTA-W₁₂ are confined to the hydrophilic planes containing the POMs, CTA⁺ cationic head-groups and water (Figure S2), which are electrically separated by the non-conductive hydrophobic regions containing the alkyl-tails of CTA⁺. Therefore, the hydrophilic planes containing the photo-reducible W⁶⁺ and photo-oxidisable O²⁻ sites could be considered to be ‘thin-films’, which are separated by insulating organic layers. This would lead to a build-up of positive charge in these layers, likely in the form of electron-holes (h^+) in the valence-bands of O⁻, O⁰ and O⁺ sites due to X-ray induced photoionization and Coulombic explosion.^{31,32}

The proximity of the organic CTA⁺ alkyl-tails (Figure S2), to the positively charged layers containing the O⁺ groups would likely accelerate oxygen-vacancy generation due to the reaction between h^+ and C-H groups producing volatile species.^{3,5} C-N bonds within the CTA⁺ head-groups would also be especially sensitive to X-ray induced photodecomposition, further injecting electrons into the sample.^{2,3,33} It is likely that a combination of the confinement of photo-generated O⁺ species, and their proximity to oxidisable organic molecules, as well as X-ray sensitive C-N bonds, contribute to the relatively fast photo-reduction of the W⁶⁺ sites in CTA-W₁₂ observed here.

The current results show that care must be taken when analysing data collected using XPS techniques on photo-reducible metal-oxide hybrids, especially when these measurements are used to determine degrees of reduction within the sample. Many redox-active, photo-responsive oxide-containing organic-inorganic hybrids have similarly confined oxide-phases surrounded by organic species, such as surfactant-encapsulated or polymer-coated nanoparticles, nanowires and quantum-dots, and therefore would also be highly susceptible to soft X-ray induced photoreduction.³⁴⁻³⁶ In fact, we recently observed that more transmissive hard X-rays (18 keV) from a synchrotron source induced disorder and coloring of the POMs in CTA-W₁₂, likely through decomposition of the structure supporting CTA⁺ amphiphiles by X-ray induced photo-redox processes between the inorganic and organic components²⁹. Efforts should be made to minimize X-ray induced damage in samples containing photo-reducible metal-cations, such as reducing total incident X-ray flux, or cryogenic cooling of the sample.^{1,8,37} If these methods are not possible or insufficient, then comments of final-states should be compared with spectra of as-prepared samples, with quantitative determinations of Mⁿ⁺/M⁽ⁿ⁻¹⁾⁺ ratios being tentative.

Conclusions

The progressive reduction of a surfactant-polyoxometalate hybrid due to repeated XPS scans was investigated. Tungsten centres within the compound were progressively reduced, as evidenced by the growth of W⁵⁺ and W⁴⁺ species at the expense of W⁶⁺. This manifested in the W4f spectrum as a shift of the combined W4f_{7/2} and W4f_{5/2} doublets to lower binding-energy positions with increasing scan number. This change was correlated with the development of a blue color in the samples. The samples remained white if only high vacuum was applied. It is concluded that care must be taken when commenting on XPS spectra of reducible metal-oxide based organic-inorganic hybrid materials due to the inevitable photoreduction of samples during the acquisition time.

This work will enable researchers studying group V and VI transition metal-oxide hybrid materials to better understand X-ray derived data of their samples. The insights gained are particularly relevant to the study of photochromism and photocatalysis.

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