Useful X-ray Photoelectron Spectroscopy-Based Chemical Tool: Differential Charging Studies of Complex Composite Materials

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ABSTRACT: Traditional X-ray photoelectron spectroscopy can inadvertently indicate the presence of two or more oxidation states for metal(s) in certain polycrystalline phase pure metal-oxides. We attribute this behavior to differential charging of samples. By employing an external bias, DC or AC, to the sample holder during spectral acquisition, we were able to minimize charging effects and determine properties dependent on grain/grain and substrate/grain interactions of complex composite polycrystalline materials.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) holds a crucial position in surface science as a powerful and widely used tool for extracting chemical and structural information on the nanometer scale due to its ability to resolve chemical identity via photoemission. While the emission is a weak process, a continuous current of 0.1–20 nA flows from the sample, resulting in an unwanted positive charge buildup on poorly conducting samples. The effect results in spectral shifts toward higher binding energies and is prominent in nonconductive samples or parts of surface heterostructures. In a sample of uniform composition, the shift can easily be compensated for by using an appropriate reference, but layered and otherwise heterogeneous materials will experience differential charging which cannot be corrected for in a simple manner. While the problem can be partially resolved using an electron flood gun, complete neutralization of the surface is difficult as attempts to replenish electrons can cause the buildup of negative charge or nonuniform charging of the sample. When varied in a controlled manner, differential charging can be used to derive chemical and/or physical parameters of composite samples. This approach, pioneered by Suzer and co-workers, has been effective but not widely used to examine differential charging and the dynamics of charge transfer in complex composite samples.

In this work, we present an experimental technique to obtain accurate XP spectra of complex composite powdered or polycrystalline materials, employing delafossites, simple insulating oxides, and gold particles (of approximate diameter 250 μm) as examples. We show that (a) it is possible to correct for unwanted charging in these samples by application of a DC external bias, (b) a two-layer structure with two key interfaces determines the charging behavior of these samples, and (c) on application of an AC external bias, information regarding charge transfer processes from the substrate (i.e., carbon tape in the current work) to the sample and within the sample itself can be extracted.

EXPERIMENTAL SECTION

Materials. Phase pure polycrystals of Nb-TiO2 and a honeycomb delafossite (Cu3Ni2SbO6) used in this study were prepared using solid-state synthesis methods. These materials have been well-characterized by X-ray diffraction (Supporting Information), XPS, and optical as well as magnetization measurements. Reagent grade powdered SiO2 (Alfa Aesar, 99.8%), polycrystalline Al2O3 (Sigma-Aldrich, 99.998%), and gold (Sigma-Aldrich, 99.9%) were also used in this work.

X-ray Photoelectron Spectroscopy. A VG ESCA Lab MkII instrument using Mg Kα (1253.6 eV) non-monochromatized radiation with an analyzer pass energy of 20 eV was used for all XPS measurements. The instrument has a two-point calibration to the Au 4f7/2 (84.0 eV) and Cu 2p3/2 (932.7 eV) peaks. Individual samples were not calibrated as the current investigation involves differential charging that cannot be compensated for by using a simple reference. Peaks were fit using the CASA XPS software and a Shirley background subtraction. Standard values for area/position constraints as well as relative intensities of spin orbit components were employed.

When probing charging properties, the samples were subjected to a ±10 V DC bias or square wave AC pulses with frequencies in the 1 mHz to 10 kHz range. The sample holder was isolated from the spectrometer ground, and the samples were electrically connected from the bottom to the sample holder using carbon or copper adhesive tape. The bias was then applied through the ground connection.

Secondary Electron Microscopy (SEM). SEM images were obtained using a Quanta 200 FE-ESEM (at 10 kV, aperture 3). The instrument’s low vacuum and ESEM modes were used to correct for
quality loss caused by charge buildup. Energy dispersed X-ray spectroscopy (EDS) was used to confirm uniformity. Samples were not coated before analysis. The sample powder was dispersed onto the carbon (or copper) tape adhered to the metal stub and pressed with a spatula for better contact between the sample and the tape. The stub was then tapped repeatedly to remove any loosely bound powder. Samples were made under identical conditions for XPS and SEM analysis.

### Differential Charging under DC and AC Bias

The XPS spectra of SiO$_2$, Al$_2$O$_3$, Au, and Nb-TiO$_2$ powder mounted on carbon tape are shown in Figure 1. XPS of the Au and Nb-TiO$_2$ samples show the presence of at least two species with X-ray diffraction (XRD) patterns corresponding to phase-pure materials (Supporting Information) difficult to explain. While XPS of Al$_2$O$_3$ and SiO$_2$ shows the presence of a single aluminum and silicon species, the binding energies do not correspond to the expected oxidation state of Al or Si. These unexpected results led us to consider the presence of differential charging during spectral acquisition.

**DC Bias.** To test the presence of charging effects in these complex samples, XPS spectra were obtained with the sample holder biased by a positive and a negative DC voltage (Figure 1). On application of a positive voltage (+10 V), the XPS spectra of polycrystalline Nb-TiO$_2$ and gold show a single central metal species with appropriate peak positions. On application of a negative voltage (−10 V), further separation of the apparent oxidation states can be observed. Such changes in the XPS spectra with respect to the applied bias prove the presence of differential charging. In conclusion, we show that application of positive bias eliminates the second oxidation state through charge neutralization.

And Nb-TiO$_2$ samples show the presence of at least two species for the central metal. Such presence of multiple species in compounds with X-ray diffraction patterns corresponding to phase-pure materials is difficult to explain. While XPS of Al$_2$O$_3$ and SiO$_2$ show the presence of a single aluminum and silicon species, the binding energies do not correspond to the expected oxidation state of Al or Si. These unexpected results led us to consider the presence of differential charging during spectral acquisition.

**AC Bias.** To test the presence of charging effects in these complex samples, XPS spectra were obtained with the sample holder biased by a positive and a negative DC voltage (Figure 1). On application of a positive voltage (+10 V), the XPS spectra of polycrystalline Nb-TiO$_2$ and gold show a single central metal species with appropriate peak positions. On application of a negative voltage (−10 V), further separation of the apparent oxidation states can be observed. Such changes in the XPS spectra with respect to the applied bias prove the presence of differential charging. In conclusion, we show that application of a positive DC bias to the sample can obviate charging effects in polycrystalline materials during XPS.

To determine the origin of the differential charging effects, powdered polycrystalline Cu$_3$Ni$_2$SbO$_6$ was investigated in detail. The Cu 2p region of the sample is illustrated in Figure 2. A DC bias of +10 V or −15 V was applied to the sample holder, after which the shift in both sets of peaks was measured in relation to a grounded (GRND) reference spectrum. Under the influence of a −15 V bias, two significant changes can be identified: the doublet peak separation increased, and the leftmost peak shows a broadened FWHM (Figure 2). Note that the latter corresponds to the highest binding energy and subsequently the system containing the highest concentration of positive charge. Focusing on the rightmost peak, the shift is exactly 15 eV to a lower binding energy, which corresponds to the trivial shift caused by the voltage-induced acceleration of all electrons toward the detector. This result is clear evidence that the low binding energy system is electrically connected to the sample holder and does not build up charge. The system corresponding to the leftmost peak, however, does not share this connection with the holder, and the increasing charge concentration caused by the negative bias cannot be replenished, as evidenced by the broadening of the peak as well as shift toward a higher binding energy. Under a +10 V positive bias, the two systems collapse into one peak and shift exactly 10 eV to a higher binding energy, again corresponding to the trivial shift (Figure 2). The stray electrons attracted toward the surface have now neutralized the positively charged surface, and the two systems merge into one peak whose position is solely dependent on the chemical identity of the sample. Thus, the data indicate the presence of a two-layer structure with one layer in good electrical contact with the sample holder and the other positioned on top of the former. This layer is unable to completely compensate for the X-ray induced charging, as it is not in sufficient electrical contact with the under-layer and, in extension, the sample holder.

Two key areas can be identified: the grain/grain and the grain/substrate interfaces. We showed that one system is in close contact with the sample substrate and can thus have its electrons replenished from the ground connection. The other system is located above the first and can be discharged only by attracting stray electrons from within the vacuum chamber. A strong barrier to charge transfer must exist between the two, even though they are in physical contact.

**AC Bias.** To probe the charge dynamics across the grain/grain interface, a second study of the Cu$_3$Ni$_2$SbO$_6$ sample was performed using a dynamic (AC) external bias. We apply a square waveform of 10 V peak to peak at various frequencies (Figure 3a). At 50 Hz the separation between the two sets of peaks (corresponding to 0 V and +10 V respectively) is exactly...
10 eV. At high frequencies, the sample does not have time to charge and discharge, and the capacitance is bypassed, reflecting only the overall resistance of the sample. This results in a set of identical peaks with an increased full width at half maximum (fwhm) at 50 Hz. As the frequency is decreased, the leftmost set of peaks (corresponding to the +10 V state of the square wave) becomes narrower, saturating around 1 Hz. Simultaneously, the set of peaks corresponding to the 0 V state starts to separate and approach the ground scan binding energies, as seen in Figure 2. The same phenomenon is observed for Au particles mounted on carbon tape (Figure 3b).

We can now measure the rate of charge transfer between the two layers by identifying the point at which charge saturation has occurred. In our case, we can confidently say that the binding energy differences become constant in the 1–0.1 Hz region, indicating the charge transfer rate to be slow, on the order of 1–10 s.

**SAMPLE AND SUBSTRATE DEPENDENT CHARGING EFFECTS**

To probe the importance of the grain/grain interface, XPS studies were conducted on a 1/4 in. pellet made by pressing the Nb-TiO$_2$ powder in a hydraulic press and at a 1 ton pressure; pellets were mounted on carbon tape. We expected that the charging effects between the grain boundaries would be minimal in a pellet due to intimate grain–grain contact. In line with the previous statement, the XP spectra of the pellets did not exhibit any charging related issues, as shown in Figure 4A. These results suggest that an increase in the grain–grain interaction can lead to a decrease in sample charging during XP spectral acquisition.

![Figure 3](image1.png)

**Figure 3.** (a) Cu$_2$Ni$_5$SbO$_6$ and (b) gold under AC bias. For both panels a and b, the frequency dependent binding energy difference revealing two electrically distinct systems saturate around 1 Hz, indicating that the charge dynamics are slow, on the order of 1–10 s.

![Figure 4](image2.png)

**Figure 4.** (a) The grain/grain interface can be modified by pressing the powder into a pellet, effectively eliminating the barrier to charge transfer. (b) The substrate/grain interface is modified by use of a copper tape substrate, resulting in the under-layer losing its electrical connection to the sample holder.

The grain/substrate interface was in turn investigated by evaluating the effect of the substrate used. The effect of using copper instead of carbon tape is illustrated in Figure 4B. The peak splitting on carbon tape is difficult to deconvolute but shows the clear presence of more than one system with respect to charging. On copper tape, this is no longer the case; instead, we see a broadened fwhm compared to that on the pellet in Figure 4A. The peaks are also positioned at a higher binding energy. Under a negative bias, the peaks shift to higher binding energies without introducing a split, indicating that we are now dealing with a homogeneous system charging together as an average entity. There is no indication that the two-layer structure is still present, demonstrating an apparent substrate dependence of this phenomenon. The substrate/grain interface thus appears to be equally important and will be the focus of a later study.

To further probe the formation of the separately charging systems, a SEM study of the powders on carbon tape was performed. The image of the carbon tape shows features with a size of 100–200 μm (Figure 5). Interestingly, the grain size of Cu$_2$Ni$_5$SbO$_6$ is two orders of magnitude smaller, while grain size of SiO$_2$ is larger than that the carbon tape features. We speculate that the substrate/grain interaction could be dependent on the relative feature size of the substrate and grain size of the mounted material. This will be probed further in a future study.
CONCLUSION

We applied an external bias to the XPS sample holder during spectral acquisition to probe the charging properties of polycrystalline materials. We identified the presence of a two-layer structure attributed to an under-layer in good electrical contact with the substrate and an over-layer electrically disconnected from the former. We illustrated how to correct the problem using a positive bias and electrons naturally present within the UHV chamber. We also identified the split to be substrate/grain as well as grain/grain interface dependent and applied dynamic bias to determine the charge dynamics to be slow, on the order of 1–10s.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b00621.

Powder XRD data for Nb:TiO₂ and Cu₃Ni₂SbO₆ samples (PDF)

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Notes

The authors declare no competing financial interest.

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Figure S. SEM images of (a) Cu₃Ni₂SbO₆ with grain size ~2 μm, (b) SiO₂ with grain size larger than 200 μm, and (c) carbon tape with groove size less than 200 μm.
