1.13: X-ray Photoelectron Spectroscopy

XPS Analysis of Modified Substances

Introduction

X-Ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is one of the most widely used surface techniques in materials science and chemistry. It allows the determination of atomic composition of the sample in a non-destructive manner, as well as other chemical information, such as binding constants, oxidation states and speciation. The sample under study is subjected to irradiation by a high energy X-ray source. The X-rays penetrate only 5 – 20 Å into the sample, allowing for surface specific, rather than bulk chemical, analysis. As an atom absorbs the X-rays, the energy of the X-ray will cause a K-shell electron to be ejected, as illustrated by Figure 1.13.1. The K-shell is the lowest energy shell of the atom. The ejected electron has a kinetic energy (KE) that is related to the energy of the incident beam (hv), the electron binding energy (BE), and the work function of the spectrometer (φ) (1.13.1). Thus, the binding energy of the electron can be calculated.
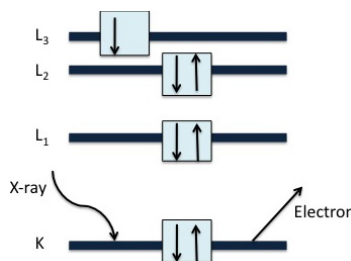

Figure 1.13.1 Excitation of an electron from an atom's K-shell.

$$BE = h\nu - KE - \psi_s \tag{1.13.1}$$

Table 1.13.1 shows the binding energy of the ejected electron, and the orbital from which the electron is ejected, which is characteristic of each element. The number of electrons detected with a specific binding energy is proportional to the number of corresponding atoms in the sample. This then provides the percent of each atom in the sample.

Table 1.13.1 Binding energies for select elements in their elemental forms.

Element	Binding Energy (eV)
Carbon (C) (1s)	284.5 - 285.1
Nitrogen (N) (1s)	396.1 - 400.5
Oxygen (O) (1s)	526.2 - 533.5
Silicon (Si) (2p)	98.8 - 99.5
Sulfur (S) ($2p_{3/2}$)	164.0 - 164.3
Iron (Fe) ($2p_{3/2}$)	706.8 - 707.2
Gold (Au) ($4f_{7/2}$)	83.8 - 84.2

The chemical environment and oxidation state of the atom can be determined through the shifts of the peaks within the range expected (Table 1.13.2). If the electrons are shielded then it is easier, or requires less energy, to remove them from the atom, i.e., the binding energy is low. The corresponding peaks will shift to a lower energy in the expected range. If the core electrons are not shielded as much, such as the atom being in a high oxidation state, then just the opposite occurs. Similar effects occur with electronegative or electropositive elements in the chemical environment of the atom in question. By synthesizing compounds with known structures, patterns can be formed by using XPS and structures of unknown compounds can be determined.

Table 1.13.2 Binding energies of electrons in various compounds.

Compound	Binding Energy (eV)
COH (C 1s)	286.01 - 286.8

Compound	Binding Energy (eV)
CHF (C 1s)	287.5 - 290.2
Nitride (N 1s)	396.2 - 398.3
Fe_2O_3 (from O, 1s)	529.5 - 530.2
Fe_2O_3 (from Fe, $2p_{3/2}$)	710.7 - 710.9
FeO (from Fe $2p_{3/2}$)	709.1 - 709.5
SiO_2 (from O, 2s)	532.5 - 533.3
SiO_2 (from Si, 2p)	103.2 - 103.9

Sample preparation is important for XPS. Although the technique was originally developed for use with thin, flat films, XPS can be used with powders. In order to use XPS with powders, a different method of sample preparation is required. One of the more common methods is to press the powder into a high purity indium foil. A different approach is to dissolve the powder in a quickly evaporating solvent, if possible, which can then be drop-casted onto a substrate. Using sticky carbon tape to adhere the powder to a disc or pressing the sample into a tablet are an option as well. Each of these sample preparations are designed to make the powder compact, as powder not attached to the substrate will contaminate the vacuum chamber. The sample also needs to be completely dry. If it is not, solvent present in the sample can destroy the necessary high vacuum and contaminate the machine, affecting the data of the current and future samples.

Analyzing Functionalized Surfaces

Depth Profiling

When analyzing a sample (Figure 1.13.2 a) by XPS, questions often arise that deal with layers of the sample. For example, is the sample homogenous, with a consistent composition throughout, or layered, with certain elements or components residing in specific places in the sample? (Figure 1.13.2 b,c). A simple way to determine the answer to this question is to perform a depth analysis. By sputtering away the sample, data can be collected at different depths within the sample. It should be noted that sputtering is a destructive process. Within the XPS instrument, the sample is subjected to an Ar^+ ion beam that etches the surface. This creates a hole in the surface, allowing the X-rays to hit layers that would not have otherwise been analyzed. However, it should be realized that different surfaces and layers may be etched at different rates, meaning the same amount of etching does not occur during the same amount of time, depending on the element or compound currently being sputtered.
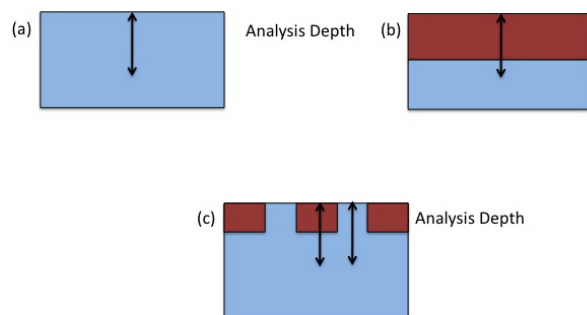

Figure 1.13.2 Schematic representation of analysis of (a) an homogeneous sample, as compared to (b) an homogeneous layers in a sample, and (c) an inhomogeneous layers in a sample.

It is important to note that hydrocarbons sputter very easily and can contaminate the high vacuum of the XPS instrument and thus later samples. They can also migrate to a recently sputtered (and hence unfunctionalized) surface after a short amount of time, so it is imperative to sputter and take a measurement quickly, otherwise the sputtering may appear to have had no effect.

Functionalized Films

When running XPS, it is important that the sample is prepared correctly. If it is not, there is a high chance of ruining not only data acquisition, but the instrument as well. With organic functionalization, it is very important to ensure the surface functional group (or as is the case with many functionalized nanoparticles, the surfactant) is immobile on the surface of the substrate. If it is removed easily in the vacuum chamber, it not only will give erroneous data, but it will contaminate the machine, which may then

contaminate future samples. This is particularly important when studying thiol functionalization of gold samples, as thiol groups bond strongly with the gold. If there is any loose thiol group contaminating the machine, the thiol will attach itself to any gold sample subsequently placed in the instrument, providing erroneous data. Fortunately, with the above exception, preparing samples that have been functionalized is not much different than standard preparation procedures. However, methods for analysis may have to be modified in order to obtain good, consistent data.

A common method for the analysis of surface modified material is angle resolved X-ray photoelectron spectroscopy (ARXPS). ARXPS is a non-destructive alternative to sputtering, as it relies upon using a series of small angles to analyze the top layer of the sample, giving a better picture of the surface than standard XPS. ARXPS allows for the analysis of the topmost layer of atoms to be analyzed, as opposed to standard XPS, which will analyze a few layers of atoms into the sample, as illustrated in Figure 1.13.3 ARXPS is often used to analyze surface contaminations, such as oxidation, and surface modification or passivation. Though the methodology and limitations are beyond the scope of this module, it is important to remember that, like normal XPS, ARXPS assumes homogeneous layers are present in samples, which can give erroneous data, should the layers be heterogeneous.
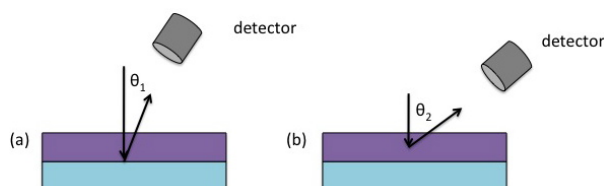

Figure 1.13.3 Schematic representation of (a) a standard XPS analysis and (b) ARXPS on a multilayer sample.

Limitations of XPS

There are many limitations to XPS that are not based on the samples or preparation, but on the machine itself. One such limitation is that XPS cannot detect hydrogen or helium. This, of course, leads to a ratio of elements in the sample that is not entirely accurate, as there is always some amount of hydrogen. It is a common fallacy to assume the percent of atoms obtained from XPS data are completely accurate due to this presence of undetected hydrogen (Table 1.13.1).

It is possible to indirectly measure the amount of hydrogen in a sample using XPS, but it is not very accurate and has to be done in a roundabout, often time consuming manner. If the sample contains hydrogen with a partial positive charge (i.e. OH), the sample can be washed in sodium naphthalenide ($C_{10}H_8Na$). This replaces this hydrogen with sodium, which can then be measured. The sodium to oxygen ratio that is obtained infers the hydrogen to oxygen ratio, assuming that all the hydrogen atoms have reacted.

XPS can only give an average measurement, as the electrons lower down in the sample will lose more energy as they pass other atoms while the electrons on the surface retain their original kinetic energy. The electrons from lower layers can also undergo inelastic or elastic scattering, seen in Figure 1.13.4 This scattering may have a significant impact on data at higher angles of emission. The beam itself is also relatively wide, with the smallest width ranging from 10 – 200 μm, lending to the observed average composition inside the beam area. Due to this, XPS cannot differentiate sections of elements if the sections are smaller than the size of the beam.
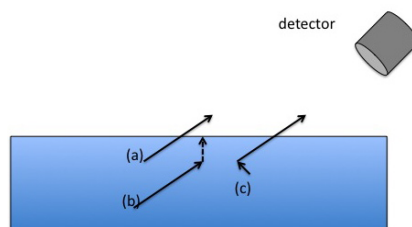

Figure 1.13.4: Schematic representation of (a) no scattering, (b) inelastic scattering, and (c) elastic scattering.

Sample reaction or degredation are important considerations. Caution should be exercised when analyzing polymers, as they are often chemically active and X-rays will provide energy to start degrading the polymer, altering the properties of the sample. One method found to help overcome this particular limitation is to use angle-resolved X-ray photoelectron spectroscopy (ARXPS). XPS can often reduce certain metal salts, such as Cu^{2+}. This reduction will give peaks that indicate a certain set of properties or chemical environments when it could be completely different. It needs to be understood that charges can build up on the surface of the sample due to a number of reasons, specifically due to the loss of electrons during the XPS experiment. The charge on the surface will interact with the electrons escaping from the sample, affecting the data obtained. If the charge collecting is positive, the electrons that have been knocked off will be attracted to the charge, slowing the electrons. The detector will pick up a lower kinetic

energy of the electrons, and thus calculate a different binding energy than the one expected, giving peaks which could be labeled with an incorrect oxidation state or chemical environment. To overcome this, the spectra must be charge referenced by one of the following methods: using the naturally occurring graphite peak as a reference, sputtering with gold and using the gold peak as a reference or flooding the sample with the ion gun and waiting until the desired peak stops shifting.

Limitations with Surfactants and Sputtering

While it is known that sputtering is destructive, there are a few other limitations that are not often considered. As mentioned above, the beam of X-rays is relatively large, giving an average composition in the analysis. Sputtering has the same limitation. If the surfactant or layers are not homogeneous, then when the sputtering is finished and detection begins, the analysis will show a homogeneous section, due to the size of both the beam and sputtered area, while it is actually separate sections of elements.

The chemistry of the compounds can be changed with sputtering, as it removes atoms that were bonded, changing the oxidation state of a metal or the hybridization of a non-metal. It can also introduce charges if the sample is non-conducting or supported on a non-conducting surface.

Using XPS to Analyze Metal Nanoparticles

Introduction

X-ray photoelectron spectroscopy (XPS) is a surface technique developed for use with thin films. More recently, however, it has been used to analyze the chemical and elemental composition of nanoparticles. The complication of nanoparticles is that they are neither flat nor larger than the diameter of the beam, creating issues when using the data obtained at face value. Samples of nanoparticles will often be large aggregates of particles. This creates problems with the analysis acquisition, as there can be a variety of cross-sections, as seen in Figure 1.13.5. This acquisition problem is also compounded by the fact that the surfactant may not be completely covering the particle, as the curvature of the particle creates defects and divots. Even if it is possible to create a monolayer of particles on a support, other issues are still present. The background support will be analyzed with the particle, due to their small size and the size of the beam and the depth at which it can penetrate.
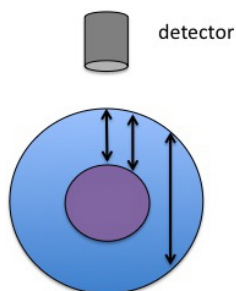

Figure 1.13.5 Different cross-sections of analysis possible on a nanoparticle.

Many other factors can introduce changes in nanoparticles and their properties. There can be probe, environmental, proximity, and sample preparation effects. The dynamics of particles can wildly vary depending on the reactivity of the particle itself. Sputtering can also be a problem. The beam used to sputter will be roughly the same size or larger than the particles. This means that what appears in the data is not a section of particle, but an average composition of several particles.

Each of these issues needs to be taken into account and preventative measures need to be used so the data is the best representation possible.

Sample Preparation

Sample preparation of nanoparticles is very important when using XPS. Certain particles, such as iron oxides without surfactants, will interact readily with oxygen in the air. This causes the particles to gain a layer of oxygen contamination. When the particles are then analyzed, oxygen appears where it should not and the oxidation state of the metal may be changed. As shown by these particles, which call for handling, mounting and analysis without exposure to air, knowing the reactivity of the nanoparticles in the sample is very important even before starting analysis. If the reactivity of the nanoparticle is known, such as the reactivity of oxygen and iron, then preventative steps can be taken in sample preparation in order to obtain the best analysis possible.

When preparing a sample for XPS, a powder form is often used. This preparation, however, will lead to aggregation of nanoparticles. If analysis is performed on such a sample, the data obtained will be an average of composition of each nanoparticle. If composition of a single particle is what is desired, then this average composition will not be sufficient. Fortunately, there are

other methods of sample preparation. Samples can be supported on a substrate, which will allow for analysis of single particles. A pictorial representation in Figure 1.13.6 shows the different types of samples that can occur with nanoparticles.
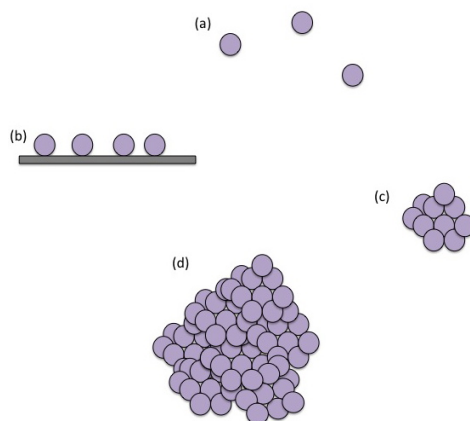

Figure 1.13.6 Representation of (a) a theoretical isolated nanoparticles, (b) nanoparticles suspended on a substrate, (c) an aggregate of nanoparticles, and (d) a powdered form of nanoparticles.

Analysis Limitations

Nanoparticles are dynamic; their properties can change when exposed to new chemical environments, leading to a new set of applications. It is the dynamics of nanoparticles that makes them so useful and is one of the reasons why scientists strive to understand their properties. However, it is this dynamic ability that makes analysis difficult to do properly. Nanoparticles are easily damaged and can change properties over time or with exposure to air, light or any other environment, chemical or otherwise. Surface analysis is often difficult because of the high rate of contamination. Once the particles are inserted into XPS, even more limitations appear.

Probe Effects

There are often artifacts introduced from the simple mechanism of conducting the analysis. When XPS is used to analyze the relatively large surface of thin films, there is small change in temperature as energy is transferred. The thin films, however, are large enough that this small change in energy has to significant change to its properties. A nanoparticle is much smaller. Even a small amount of energy can drastically change the shape of particles, in turn changing the properties, giving a much different set of data than expected.

The electron beam itself can affect how the particles are supported on a substrate. Theoretically, nanoparticles would be considered separate from each other and any other chemical environments, such as solvents or substrates. This, however, is not possible, as the particles must be suspended in a solution or placed on a substrate when attempting analysis. The chemical environment around the particle will have some amount of interaction with the particle. This interaction will change characteristics of the nanoparticles, such as oxidation states or partial charges, which will then shift the peaks observed. If particles can be separated and suspended on a substrate, the supporting material will also be analyzed due to the fact that the X-ray beam is larger than the size of each individual particle. If the substrate is made of porous materials, it can adsorb gases and those will be detected along with the substrate and the particle, giving erroneous data.

Environmental Effects

Nanoparticles will often react, or at least interact, with their environments. If the particles are highly reactive, there will often be induced charges in the near environment of the particle. Gold nanoparticles have a well-documented ability to undergo plasmon interactions with each other. When XPS is performed on these particles, the charges will change the kinetic energy of the electrons, shifting the apparent binding energy. When working with nanoparticles that are well known for creating charges, it is often best to use an ion gun or a coating of gold. The purpose of the ion gun or gold coating is to try to move peaks back to their appropriate energies. If the peaks do not move, then the chance of there being no induced charge is high and thus the obtained data is fairly reliable.

Proximity Effects

The proximity of the particles to each other will cause interactions between the particles. If there is a charge accumulation near one particle, and that particle is in close proximity with other particles, the charge will become enhanced as it spreads, affecting the

signal strength and the binding energies of the electrons. While the knowledge of charge enhancement could be useful to potential applications, it is not beneficial if knowledge of the various properties of individual particles is sought.

Less isolated (i.e., less crowded) particles will have different properties as compared to more isolated particles. A good example of this is the plasmon effect in gold nanoparticles. The closer gold nanoparticles are to each other, the more likely they will induce the plasmon effect. This can change the properties of the particles, such as oxidation states and partial charges. These changes will then shift peaks seen in XPS spectra. These proximity effects are often introduced in the sample preparation. This, of course, shows why it is important to prepare samples correctly to get desired results.

Conclusions

Unfortunately there is no good general procedure for all nanoparticles samples. There are too many variables within each sample to create a basic procedure. A scientist wanting to use XPS to analyze nanoparticles must first understand the drawbacks and limitations of using their sample as well as how to counteract the artifacts that will be introduced in order to properly use XPS.

One must never make the assumption that nanoparticles are flat. This assumption will only lead to a misrepresentation of the particles. Once the curvature and stacking of the particles, as well as their interactions with each other are taken into account, XPS can be run.