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X-ray Photoelectron Spectroscopy

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Overview

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X-ray photoelectron spectroscopy (XPS) is a technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top several nanometers of the material being analyzed (within ~ the top 10 nm, for typical kinetic energies of the electrons). Due to the fact that the signal electrons escape predominantly from within the first few nanometers of the material, XPS is considered a surface analytical technique.

The discovery and the application of the physical principles behind XPS or, as it was known earlier, electron spectroscopy for chemical analysis (ESCA), led to two Nobel prizes in physics. The first was awarded in 1921 to Albert Einstein for his explanation of the photoelectric effect in 1905. The photoelectric effect underpins the process by which signal is generated in XPS. Much later, Kai Siegbahn developed ESCA based on some of the early works by Innes, Moseley, Rawlinson and Robinson, and recorded, in 1954, the first high-energy-resolution XPS spectrum of NaCl. Further demonstration of the power of ESCA/XPS for chemical analysis, together with the development of the associated instrumentation for the technique, led to the first commercial monochromatic XPS instrument in 1969 and the Nobel Prize for Physics in 1981 to Siegbahn in acknowledgement of his extensive efforts to develop the technique as an analytical tool.

Principles

Principles of X-ray Photoelectron Spectroscopy:

In XPS, incident X-rays from a source, typically Al Kα, with photon energy of 1486.7 eV, irradiate a sample and, meeting the threshold binding energies of some (if not all) of the core electrons in the constituent atoms in a material, eject these core electrons past the Fermi energy (E_f). Al Kα is a specific X-ray fluorescence emitted during the relaxation of Al atoms that have been taken to excited states through the ejection of their 1s electrons. As we see in Figure 1, if the energy of the source X-rays (Es) is sufficiently high, then the core electron can meet the threshold work function (ϕ) needed to get past the vacuum level (E_{vac}) and emerge with remnant kinetic energy. These electrons are called photoelectrons, and provided that they are close enough to the surface, they can emerge from the surface of the sample and be picked up by an energy discriminating electron detector. Such a detector measures the kinetic energy of the photoelectron (KE), which can be used to calculate the binding energy (BE) of the electrons:

$BE = E_S - \Phi - KE$

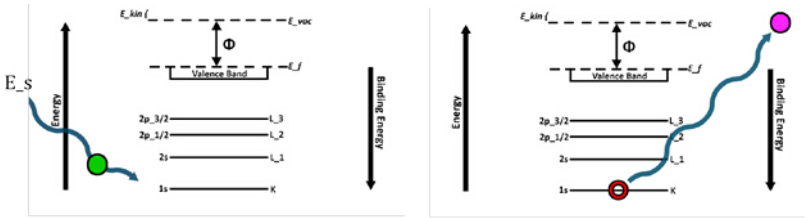

Figure 1: Illustration of the principles of XPS.

Because the inelastic mean free path (IMFP) of the signal electrons is only a few nanometers (i.e. the average distance that electrons travel between inelastic scattering events is a few nanometers XPS requires ultra-high vacuum (UHV) conditions within the measurement chamber.The detection limits for most of the elements are on the order of parts per thousand range (1,000 PPM). In order to achieve better detection limits of parts per million (ppm), the technique requires either a high concentration of the species being detected at top surface or very long collection time (multiple hours). The resulting data will be in the form of a spectrum where an intensity (representing the counts per second of electrons hitting the detector) versus the binding energy. Provided that the X-ray source is energetic enough to eject electrons from particular electronic states of the atoms in the material (e.g. the valence band and the L3 level in Figure 1) there will be one or more corresponding peaks in the spectrum. The BE of a certain peak of an element in the spectrum can then be compared to those of reference materials, or to tabulated values in databases, in order to determine the "chemical state" of that element in the sample. The intensity of a certain elemental peak is, of course, proportional to the concentration of that element in the sample. However, because the probabilities of ionizing different electron states vary, the conversion of the measured counts under spectral peaks to concentrations values will require the normalization of the counts by "sensitivity factors" that corrects for these differing probabilities.

The XPS system can accommodate thin films, bulk samples up to ~ 1cm thick, and powder samples. The sample stage here is 60 mm by 60 mm and can hold as many samples as will fit into this area. Films can be inorganic or organic/biological as long as they are dry.

Procedure

1. The sample is a thin film of Pt (3 atomic layers thick) grown on a single layer of graphene, which is supported on a commercial silica (SiO_2) glass slide. The graphene (which is a single layer of carbon) was grown on Cu and then transferred to the glass substrate. The Pt atomic layers were then deposited by electrodeposition methods.
2. To load the samples, first vent the loadlock (see the schematic drawing in **Figure 2**) to get the sample holder. Make sure to follow cleanliness rules for UHV systems. These include: no bare skin, hair, or moisture in contact with samples or sample holder. Use clean tweezers to handle your sample. The door of the loadlock will spring open after the loadlock chamber has vented to atmospheric pressure (~5 minutes). Take out the sample holder.

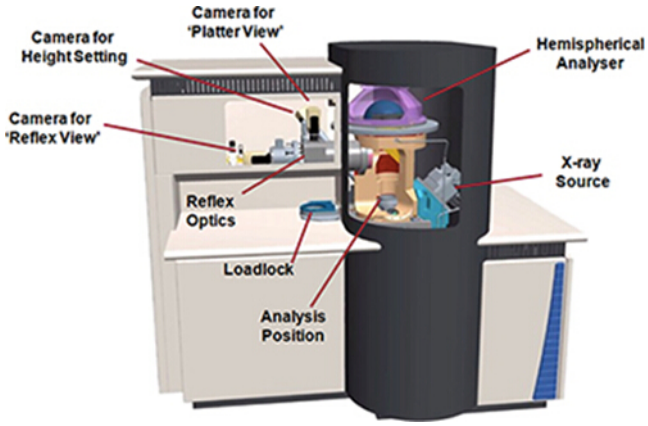

Figure 2: Schematic of XPS instrument.

3. The sample is held by the spring clips which should be on the stage. Wipe down the stage surface and the clips you are using with alcohol and dry completely.
   a.Open the loadlock door and put the sample holder back on the transfer arm. The holder will only fit correctly one way.
   b.Close the door and pump down the load lock for about 10 minutes, although you may need extra pumpdown time for some samples (e.g., if it is highly porous, a powder, or contains some unevaporated solvent) and then transfer the sample into the analysis chamber. Note the analysis chamber pressure when the sample transfer occurs. It should be in the mid-to-low 10^{-7} mbar range then drop rapidly into the 10^{-8} mbar range when the valve between the two chambers closes.
4. Check the analysis chamber pressure. It should be in the mid 10^{-8} mbar range or below when an experiment is started.
5. Set the pass energy. The pass energy is the energy with which all the photoelectrons will enter the spectrometer and ensure that all the features measured in the spectrum have the same energy resolution. This is because the energy resolution of the spectrometer, ΔE, scales with kinetic energy of the photoelectrons, and so having a constant energy for all electrons entering the detector sets a constant resolution for the whole spectrum. The higher the pass energy, the higher the flux of electrons entering the detector and, thus, better signal-to-noise ratio (s/n), but this comes at a cost of worse energy resolution (larger ΔE). Conversely, a lower pass energy ensures a better energy resolution but at a cost of lower flux and, therefore, a lower s/n.
6. Collect a survey spectrum. Here your goal is to capture all the various types of electrons that are being ejected from the sample, and be able to, therefore, survey the elemental content of your sample. The detector (spectrometer) will therefore have to be set up to try and capture as many of these types of electrons as possible. You can do this by setting the widest energy scan range for the spectrometer. The specific software controls will vary for the different commercial XPS systems. The survey spectrum allows you to inspect all the photoelectron emissions within your sample prior to doing a high-resolution scan on specific emissions.
7. For our representative spectrum we have an SiO_2 supported architecture, that also contains C and Pt. The Pt, Si, C and O core-level peaks are labeled in the survey spectrum (**Figure 3**). Due to the ubiquity of water, oxygen and hydrocarbon molecules in air, a certain amount of these molecules are always expected to be physically or chemically adsorbed on the surface of any sample, and so a C and O signal is almost always expected.
8. Collect the characteristic core level spectra of your material. Here as the representative spectrum, we show the 4f spin-orbit split peaks for Pt.

Results

Figure 3 shows a survey spectrum from the sample, clearly showing the Pt, Si, C and O emissions. In **Figure 4**, we see the high resolution scan of the Pt $4f_{7/2}$ and $4f_{5/2}$ peaks from the sample. The binding energies of each of the core level peaks can be compared to those found in databases such as the one maintained by the National Institute of Standards and Technology (NIST) (at https://srdata.nist.gov/xps/Default.aspx). The subtle shifts in binding energy relative to those of the reference compounds in the database can reveal the chemical state of each of the elements in your sample. The intensity ratio of the peaks will reveal the surface composition.

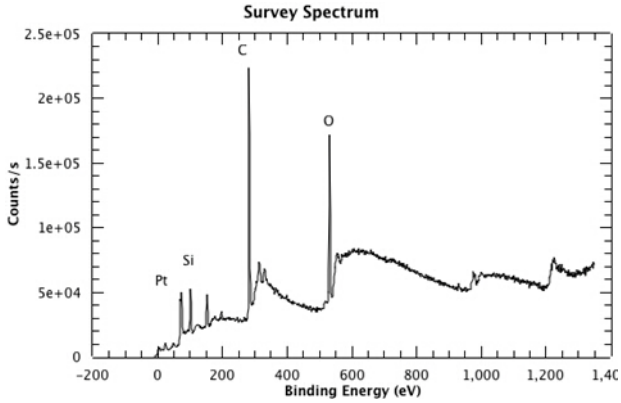

Figure 3: A survey spectrum from the sample, clearly showing the Pt, Si, C and O emissions.

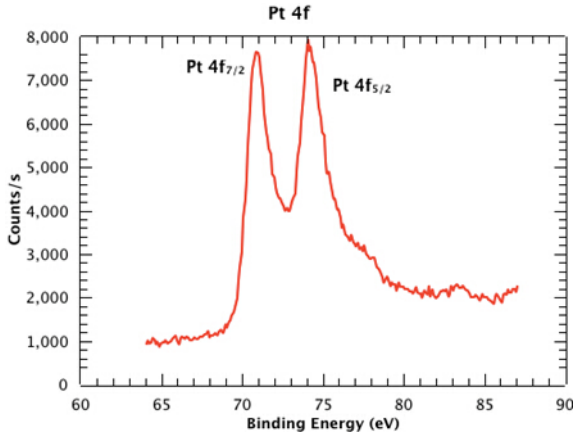

Figure 4: High resolution scan of the Pt $4f_{7/2}$ and $4f_{5/2}$ peaks from the sample.

Applications and Summary

XPS is a surface chemical analysis technique that is versatile in the range of samples it can be used to investigate. The technique provides quantification of chemical composition, chemical state and the occupied electronic structure of the atoms within a material.

XPS provides elemental the composition of the surface (within 1-10 nm usually), and can be used to determine the empirical formula of the surface compounds, the identity of elements that contaminate a surface, the chemical or electronic state of each element in the surface, the uniformity of composition across top surface and through the depth (by sequentially milling into the material and taking XPS data of the new exposed surface).

Routinely, XPS is used to analyze a wide range of materials, for example metal alloys, other inorganic compounds such as ceramics, polymers, semiconductors, catalysts, glasses, parts of plants biological materials such as cells, bones and many others.