XPS protocol for the characterization of pristine and functionalized single wall carbon nanotubes.

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Abstract:

Recent interest in developing new applications for carbon nanotubes (CNT) has fueled the need to use accurate macroscopic and nanoscopic techniques to characterize and understand their chemistry. X-ray photoelectron spectroscopy (XPS) has proved to be a useful analytical tool for nanoscale surface characterization of materials including carbon nanotubes. Recent nanotechnology research at NASA Johnson Space Center (NASA-JSC) helped to establish a characterization protocol for quality assessment for single wall carbon nanotubes (SWCNTs). Here, a review of some of the major factors of the XPS technique that can influence the quality of analytical data, suggestions for methods to maximize the quality of data obtained by XPS, and the development of a protocol for XPS characterization as a complementary technique for analyzing the purity and surface characteristics of SWCNTs is presented. The XPS protocol is then applied to a number of experiments including impurity analysis and the study of chemical modifications for SWCNTs.

Introduction:

The unique properties of single-walled carbon nanotubes may enable the development of materials with vastly improved properties for a variety of applications for human spaceflight [1-3]. Often, these carbon nanotubes must be chemically modified in order to tailor them for specific applications. Characterization of the raw and modified SWCNTs is the important first step in monitoring the processes for purification as well as designing and developing new materials. At present, the NASA-JSC protocol [4] provides one first step in SWCNT characterization data and additional techniques are needed to supplement this information. X-ray Photoelectron Spectroscopy (XPS) can provide information complementary to that generated by the existing NASA-JSC protocol.

XPS has proved to be a useful analytical tool for monitoring the processing steps by providing information on the relative amounts of different elements with respect to carbon and their valence states. Since other analytical techniques cannot distinguish between the sp^2 and sp^3 carbons very well, XPS can be useful in the semi-quantitative analysis of carbon species in SWCNT materials. However, because XPS is a primarily a surface sensitive technique, it is not suitable for bulk analysis of materials. As a result, XPS has not been as widely used as other techniques to characterize carbon nanotubes. XPS may however be used to monitor the presence of other elemental species within the material or their influence on the carbon atoms. In fact, many of the investigations on carbon nanotubes that utilize XPS have been focused on chemical modifications of SWCNTs [5-7]. In some cases, XPS has been used to identify the type of bonds that attach functional groups to SWCNTs [8]. It would therefore be helpful to understand the advantages and limitations of XPS in order to successfully apply it toward the characterization of SWCNTs.

1.1 General Description:

XPS is an analytical technique that can be used not only for elemental identification within a sample but also for identifying the oxidation state of the element [9, 10]. It can be used to investigate such areas as corrosion, oxidation, surface contamination and modification, absorption and deposition of chemical species, catalysis and many other nanoscale surface processes. The general principle of XPS is the measurement of the energy of inner-shell electrons that have been emitted from atoms by a photo-ionization process. Because of its sensitivity and its reliance on the photo-ionization effect, XPS requires ultra high vacuum conditions. The major components of XPS are an ionization source and an energy analyzer, although other components are generally implemented to provide additional capabilities. A general schematic of an XPS system and its primary components is shown in figure 1.

1.1.1. Instrumental Components and Operating Principles:

XPS uses low energy x-ray photons to eject core-shell electrons from the atoms within a solid and these electrons are subsequently characterized by their energies. The energy of the emitted electron is characteristic of the atom from which it was emitted. The chemical environment surrounding an atom can cause deviations in the energy of the emitted electron due to changes in the binding energy of the emitted electrons. These deviations allow for chemical state identification. In order to reliably interpret XPS data of carbon nanotubes, knowledge of the influence of instrument components as well as operating conditions on XPS spectra is beneficial.

1.1.2 Ionization Sources and Beam Sizes:

X-ray sources used in XPS can be single or dual ionization sources as well as monochromatic depending on the system. Dual X-ray sources generally consist of an aluminum

and magnesium anode and are not monochromatic. The advantage of a dual X-ray source is that it allows differentiation between Auger and photoelectron peaks in XPS spectra. In a multi-element system, Auger signals may overlap or interfere with photoelectron peaks, resulting in the misinterpretation of XPS spectra [10]. On the other hand, monochromatic X-ray sources can be advantageous because they provide greater energy resolution along with reduced background signal [10], since they provide a narrower line width and the elimination of satellites as well as Bremstralung emissions from the X-ray source. This increased energy resolution can be particularly favorable for evaluating carbon peak in SWCNTs, in particular, for differentiating between the sp^2 and sp^3 hybridized carbon that can be present. Furthermore, greater energy resolution is important for identifying the chemical states of elements associated with the SWCNTs (i.e. functionalization). This is especially true if the binding energy difference between the chemical species is on the order of the energy separation between the $K_{\alpha,1}$ and $K_{\alpha,2}$ component of the primary X-ray emission line. The use of a monochromatic source is recommended for SWCNT characterization because of greater reliability in spectral interpretation.

Regardless of the type of X-ray source, spatial resolution is limited due to the difficulty in focusing the ionization beam to a small area. Modern advancements in X-ray optical lenses allow the focusing of X-rays to beam sizes down to several microns, thus increasing the spatial resolution. For systems not equipped with focusing lenses, the typical spot size of the X-ray beam is on the order of 3-5mm^2 depending on how close the X-ray source can be moved towards the sample. The increased spatial resolution allows for better line scan and area profiling analysis. For systems where the X-ray source cannot be focused to the micron scale, an alternative approach is to lower the acceptance angle of the entrance aperture to the energy

analyzer, which essentially increases the spatial resolution by decreasing the analysis area [7, 11]. However, decreasing the acceptance angle will consequently reduce the signal intensity. Although this technique is incapable of characterizing individual SWCNTs (because the dimension of a single SWCNT is far below the capable spatial resolution of XPS) the spatial resolution may be adequate for examining particle dispersion, pattern deposition or bulk functionalization in materials. Auger spectroscopy should be considered when higher spatial resolution is required.

1.1.3 Energy Analyzers and Pass Energy

Electron energy analyzers are used to measure the electrons that are photoemitted from the surface upon X-ray bombardment. Energy analyzers are defined by their collection efficiency and their energy resolution. The collection efficiency is a measure of the photoelectrons detected to those emitted, while the energy resolution is the ability to distinguish between electrons with closely separated energies. The energy resolution is defined as a constant determined by the geometric configuration of analyzer and can further be related to the pass energy as $\Delta E/E$ = constant, where E is the pass energy and ΔE is the energy resolution. The pass energy controls which electrons reach the detector, by defining the kinetic energy which electrons must possess in order to pass through the analyzer. Electrons within this range will pass through the analyzer while all others will be deflected. Large pass energies are desirable for weak signals so that the energy analyzer can accept more electrons thereby increasing the signal intensity. Conversely, decreasing the pass energy effectively reduces the signal intensity, but increases the resolution. Thus when detection of a chemical species is the major interest large pass energies should be used so as to maximize the signal. On the other hand when identifying the chemical state of analytes, smaller pass energies are suggested for increased reliability.   In

SWCNT characterization the type of information desired determines the choice of pass energy. For example, large pass energies would be recommended to monitor the degree of functionalization so that small degrees of functionalization may be detected. For impurity analysis or particle deposition, small pass energy should be used to correctly evaluate the oxidation states of the moieties.

The two common types of energy analyzers that are used in XPS are the cylindrical mirror analyzer (CMA) and the hemispherical energy analyzer (HEA). Both have a transmission efficiency, which is inversely related to the kinetic energy of the emitted electrons and will influence the signal intensities [9]. In addition, each element has an ionization cross section which also contributes to the sensitivity of XPS to a particular element. This sensitivity factor is important when using XPS for quantitative analysis. CMA has the advantage of better collection efficiency because it can be positioned in closer proximity to the sample, while HEAs provide better energy resolution but are located further from the sample, resulting in lower collection efficiency. The advantage of the HEA in SWCNT characterization is the enhanced resolution, which is better suited for resolving the different species of carbon. Although CMA has lower energy resolution than the HEA, the resolution of the CMA can be increased by use of a double pass configuration [9]. A CMA may be advantageous in situations where the species of interest is in low concentration, thereby producing a weak signal.

1.1.4 Neutralizer and Sputter Guns

Surfaces of materials are inherently covered with contaminants, primarily oxygen and nitrogen due to exposure to atmosphere, which may lead to miscalculated atomic percentages or obstruction of spectral peaks if not removed or accounted for during analyses. These contaminants can easily be removed through ion sputtering or annealing [12-16]. Sputtering is

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accomplished by bombarding the surface with energetic (5-10 keV) argon ions. In addition to contaminant removal, ion sputtering also provides the ability to do depth profiling and can be used to assess any differences in chemical or elemental changes between surface and bulk [5, 17]. All XPS systems are equipped with an ion sputter gun for contaminant removal.

Some of the factors that should be considered with ion sputtering are etch rates, sputter area, preferential sputtering, and ion implantation [10]. The etch rate depends on several factors including the mass of the element, the bond strength, the beam current, the energy of the sputtering ion (Ar) and the area over which the beam is rastered [18]. Since the rate is dependent on atomic mass and bond strength, preferential sputtering can occur. This becomes more significant for very short duration sputter times. Another consideration in ion sputtering is that the minimum beam size is on the order of 1-2mm^2. The sputtering area will possess some curvature which can be more significant if the sample surface is not truly perpendicular to the ion beam trajectory. This is important to consider when the beam size of the X-ray source is on the order of the ion beam sputter area. Finally, sputtering ions can be implanted into the surface of the material, thus contributing to the XPS signal. All of these factors should be accounted for when calculating atomic percentages or in doing depth profiling.

With SWCNT characterization, thoughtful consideration into the effects of sputtering should be addressed before performing the experiment, since species of interest may be removed, producing inaccurate elemental evaluations. Sputtering, for example, could significantly influence the determination of the degree of functionalization of the carbon atoms of SWCNTs. A good rule of thumb is to always obtain spectra prior to any ion sputtering.

When electrons are removed from a solid surface, non-conductive samples can develop an electron deficiency producing a positive charge build-up at the surface. Sample charging can

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often be eliminated by an electron neutralizer gun [9, 19-21], which uses a beam of low energy electrons to compensate the positive charge. The only requirement is that enough current is supplied to the sample to balance the charge build up. Charge referencing [22, 23] is recommended to ensure proper charging compensation. In charge referencing, a particular element such as Au or adventitious carbon are used as the reference to determine the extent of peak shifting associated with charging. For systems that are not equipped with a neutralizer gun, a thin film of conductive material [24, 25] can be deposited on the surface, which provides a pathway for electrons to the surface thus reducing the charging effect. When samples are coated ex-situ, the coating is removed from the analysis area by ion sputtering. A neutralizer gun should be used for SWCNT samples which are grown on nonconductive substrates, have nonconductive impurities which are of interest, or whose processing has made them non-conductive.

1.1.5   Sample Mounting and Sample Stages

The main criterion for samples being analyzed by XPS is that the sample should be compatible with high vacuum conditions. They can be conductive or non-conductive but should not decompose under irradiation. The sample holder limits sample size, while the focusing distance limits the sample height. Samples can be mounted using a variety of methods such as binding clips, adhesive tape or paint, or foils. Mounting clips may not be properly suited for all SWCNT material, in particular powders or as-produced material. Carbon tape may be used but it is not advisable when analyzing the carbon peak, not to mention the difficulty in differentiating between the tape and the SWCNT material during imaging. Copper tape is preferable since the SWCNTs are clearly imaged and no erroneous data stems from the carbon tape background. In both cases, it is crucial to ensure that powder samples completely cover the surface of the area of

interest to avoid any extraneous signals due to adhesives from the tape. Indium foil can be used for powder samples but some SWCNT materials do not readily embed themselves well into the foil. Foils and clips are the recommended form of sample mounting when possible since there will be no contribution to the carbon peak from any adhesive binders. For SWCNTs grown on non-conductive substrates such as silicon dioxide or alumina, the sample can be secured with adhesive tape and either sputter coated or silver paint can be applied along the edge of the sample to provide electrical conductivity. Such coatings, which can also be used for charge referencing, can then be removed by sputtering. Any of these mounting methods can be used so long as adequate electrical contact to the surface is ensured.

Sample stages in XPS, depending upon their design, allow mounting of multiple or individual samples. The sample stage is generally grounded but some stages allow placing a potential on the sample. The stage is generally transferred onto a variable translator which allows motion in all directions as well as rotation. This rotational ability allows angle resolved spectroscopy, which increases the surface sensitivity of the technique. Angle resolved spectroscopy is useful for assignments of carbon atoms associated with small functional groups. Finally some stage systems can also be equipped with cooling and heating capability for in-situ observation of surface changes with temperature. Such experiments are useful in SWCNT characterization for functional group stability or impurity removal determination.

1.2 Sources of Error

As with all analytical techniques, there are several sources of error that can lead to misinterpretation of XPS data. A brief discussion on the type of errors that can be encountered in XPS, along with examples of how they can influence SWCNT characterization, is provided below.

1.2.1 Surface Charging

Surface charging can have substantial effects on XPS spectra, such as broadening that increases the noise level, and shifting of photoelectron peaks [9, 19, 26]. The degree of shifting or broadening may not be the same for every element contained in the sample. This shifting and broadening can result in the inappropriate labeling of spectral features, or even falsely indicate peaks that appear to consist of species with more than one oxidation state. Although SWCNTs are conductive, charging may occur in samples that are produced or deposited on non-conductive substrates or whose surface modifications have reduced their electrical conductivity. Using an electron neutralizer gun easily compensates such charging effects. If the system is not equipped with a neutralizer gun, a thin film of gold can be deposited that can be etched away. This gold film can also be used for charge referencing to compensate for shifting effects. Figure 2. contrasts the use of coating and the neutralizer for examining SiO_2 within impurities found in the TGA ash of SWCNTs. Surface charging can be relatively straight forward to monitor with SWCNTs since the carbon peak position for graphitic type carbon is well established. However the position may shift when SWCNTs are highly doped, functionalized, or damaged. It is a good practice to acquire XPS spectra with and without a neutralizer gun to confirm that no charging has occurred.

1.2.2 Surface Contamination and Absorption

XPS is surface sensitive to probing approximately 50-100 Å of the outer surface. Thus surface contamination can produce significant errors in data analysis. Surface contaminants are inherently present in all samples that have been exposed to air. Samples should never be handled without gloves since the oil from bare hands can contaminate both the sample and the vacuum chamber. Surface contaminants can give rise to foreign species or lead to incorrect atomic

percentages by reducing the signal intensities. To reduce this error, sputtering or annealing should always be performed. Care should be taken however when sputtering since excessive sputtering can result in the removal or damage of the element of interest. In addition, ion implantation can lead to incorrect values of atomic percentages if not adjusted for in the analysis. Sputtering should be gradually performed until no change in the peak intensities is observed. Even when a sample is sputtered, absorption of gases within the chamber, likely to occur under poor vacuum conditions or during long duration data acquisition, may still influence the XPS data. Surface contamination and adsorption can be influential in SWCNT analysis particularly if one of these contains the same element as species of interest (i.e. if a functional group contains an oxygen atom which is also present in H_2O or CO_2, both typical contaminants). Absorbed gases can make it difficult to evaluate the carbon peak in SWCNTs, in particular where oxygen bound carbon species are being examined. The porous nature of the SWCNTs may allow for CO and CO_2 to be absorbed within the tubes and this can contribute to carbonyl structure of the carbon peak. Caution should be taken when quantifying carbon components. Both surface contamination and absorption should be minimized or accounted for to prevent erroneous conclusion of chemical species.

1.2.3   Resolution

The resolution of the energy analyzer can reflect on the reliability of both qualitative and quantitative analysis. If the resolution is set to low both peak assignments and quantitative determination may be inaccurate. Low resolution will reflect in a larger full width at half maximum of the photoelectron peak, and the peak width may be large enough to allow poor discrimination between possible chemical states and their quantities. On the other hand high resolution may obscure the detection of a weak signal. In SWCNT characterization, the type of

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information desired will determine the choice of resolution. Low resolution will suffice for species identification, while lower pass energy is required when selective determination of the carbon components within the same sample is required. It is good practice to obtain initial spectra with lower resolution followed by spectra centered about the species of interest with higher resolution. Regardless of the resolution selected, the signal to noise ratio (general rule is noise = square root of signal) should be maximized for proper analysis.

1.2.4 Overlapping Signals

Signal overlapping can occur in materials with multiple elements, since each element generally has more than one spectral feature associated with it. With XPS the primary emission peak is used for analysis but at times these may lie in the vicinity of secondary peaks from other elements. This can complicate the assignment of peaks to specific chemical compounds. Furthermore, overlapping can contribute to the intensity of a peak that is used in quantitative analysis thereby resulting in erroneously high atomic percentages. The experimental section discusses the effect of peak overlap errors in the analysis of impurities in SWCNTs produced by pulsed laser vaporization.

1.2.5 Ghost and Satellite Peaks

Ghost peaks usually arise from contamination of the X-ray source or from oxidation of the anode. Depending on the extent of the oxidation, photoelectron emissions can lead to shoulders on the higher binding energy side of a peak. This can be important when analyzing the C1s peak in SWCNTs. Another source of ghost peaks is cross contamination in dual anode systems, which occurs when one anode becomes contaminated from the metal of the other anode. This will produce additional peaks in the spectra. In order to avoid ghost peaks the X-ray anode should be frequently degassed.

Satellite peaks result from multiple emission lines produced during X-ray fluorescence from the anode. Satellite peaks are usually located on the lower binding energy edge of the photoelectron peaks. They originate from electrons of the same orbital energy but have kinetic energies that are higher because their emission is caused by higher energy photons. Because of their higher kinetic energy, they appear to have lower binding energy. Using a monochromatic X-ray source can eliminate these satellites. Satellite peaks can be problematic when different elements have primary peaks that are located very close to each other.

2. Suggested protocol for XPS characterization of SWCNTs:

The following protocol is proposed, taking into consideration the individual components and factors involved in the XPS characterization of SWCNTs. The exact methods, left to the discretion of the analyst, will vary depending on the type of information desired. This procedure provides a basic guideline for characterizing SWCNT material and may be extended to Auger and ultra-violet photoelectron spectroscopy.

1. Mounting clips or indium foil are the ideal methods for mounting samples. However, if the nature of the material or the sample holder restricts their use, then conductive tape can be used, with copper preferred. When using tape, the sample should completely and uniformly cover the tape surface to avoid erroneous signal arising from the background.

2. Use of a monochromatic X-ray source is suggested for high-resolution work in particularly when analyzing the carbon 1s peak. A dual anode should be used for multi-element samples where mixing of photoelectron and Auger peaks is expected, in order to maximize accuracy of quantitative chemical data. Calibrate system using the Au 4f peak from a sputtered Au sample with using high energy resolution. If errors in the calibration are found, then be sure to degas the anode.

3. For elemental analysis a large beam size and pass energy are suggested so that very low concentrations can be detected. For chemical state analysis a large beam size with a small pass energy and step increments on the order of the resolution should be used. Also for chemical state analysis localized scans of the peak of interest should be used instead of survey scans. For line scanning use a beam size on the order of the step increment.

4. Normal incident angle of 90º with respect to the analyzer entrance should be used in order to maximize signals. To characterize functionalized or modified SWCNTs, angle resolved acquisition is encouraged to obtain more reliable assessment of the degree of modification. Take off angle can be varied between 0-45º until the substrate no longer appears to contribute to the spectrum.

5. Always acquire XPS spectra prior to ion sputtering. Calculate the amount of time required to remove 1-2 monolayers of carbon, oxygen and nitrogen. For quantitative analysis continue sputtering until no variations in intensity are observed or until all undesirable species are no longer present.

6. Check for charging of samples by acquiring spectra with and without a neutralizer gun and monitor shifting of the carbon peak. If the system is not equipped with a neutralizer gun, sputter coating with Au is recommended for charge referencing. The Au can be removed by sputtering while monitoring signals until they are maximized. It is recommended that samples be analyzed with and without the neutralizer to confirm charging within samples.

7. With beam sizes of the micron scale a minimum of three locations should be analyzed to confirm that the analysis is representative of the sample. With non-focused sources where the beam size is millimeters in diameter, two scans are recommended to check for variations resulting from non-uniform coverage.

Experimental

XPS characterization was used to evaluate the levels of impurities within SWCNTs, the degree of amine functionalization and the deposition of Pt particles in SWCNTs. The above XPS protocol was used in these various aspects of SWCNT characterization. The protocol guidelines were adjusted to fit the particular needs of the SWCNT characterization.

3.1 Impurity Analysis

Thermogravimetric analysis (TGA) has been used to provide a quantitative measure of the level of metal impurities [4, 27, 28] that are inherent by-products of any SWCNT growth process [29-31]. It is largely assumed that during TGA analysis in air SWCNTs fully decompose and that the residual ash consists only of metal oxides and carbides. Traditionally, the residual ash of laser-produced SWCNTs that have been oxidized air at elevated temperature is composed of Co, Ni, and Si impurities. In order to accurately determine the metal content in SWCNT materials, XPS was performed on the TGA ash of SWCNTs produced by laser ablation [32] to determine the oxide states of the metals and check for the presence of carbide species in the ash.

XPS was performed using both a PHI Quantera XPS Microprobe with a monochromatic aluminum x-ray source or a VG ESCALAB MKII system equipped with a dual anode source. The residual ash was pressed onto two different indium foils one of which was lightly coated with a thin layer of gold-palladium. The coated sample was gradually sputtered (~5 minutes) until no Au or Pd was observed, then a survey scan (pass energy 112 eV, resolution of 0.67 eV) was obtained to identify the individual constituents within the ash. Localized scans centered about the major photoelectron peak were then obtained with lower pass energy (pass energy 55 eV, resolution of 0.33 eV). The chemical state analysis of Si is complicated because the Co 3s peak (101 eV) lies in the same region as the Si 2p peak (99 eV). This overlapping makes it

difficult to determine the exact fractions of Co, Ni and Si in the ash. A low energy electron gun was also used in order to neutralize charging which was evaluated by the position of the various peaks.

The TGA ash was retained after heating the SWCNT material in air to 1000 ºC. Figure 3 shows that the constituents of TGA ash laser-produced SWCNTs consist of Co, Ni, O, and Si. The Co is partially oxidized to CoO and possibly $Co(OH)_2$, while the Ni does not show appreciable oxidation. It was not suspected that any sputter reduction [19, 33] occurred in these samples because the peak ratio, between oxidized to reduced metal, did not appreciably change with continuous sputtering. The Si was present in the material as SiO_2 with the small shoulder on the lower energy side being attributed to the Co 3s peak and not SiC since a very weak carbon peak was located at the graphite binding energy. The SiO_2 present in the SWCNT material is attributed to the quartz production oven. The acknowledgement of the presence of SiO_2 and no oxidation of Ni will allow for a better estimation of non-carbonaceous impurity content as well as aid in purification schemes.

3.2 SWCNTs Functionalization

XPS has been used extensively in the characterization of SWCNTs subjected to functionalization and chemical modifications [34-37]. Recent work has investigated the possibility of functionalizing SWCNTs with amine bearing polymer chains for the removal of atmospheric CO_2, as part of the environmental control and life support systems in space applications [38]. In this case XPS was used to 1) indicate the functionalization of SWCNTs, 2) estimate the amount of amine loaded onto the support, as well as 3) determine the thermal stability of the solid-supported materials.

Functionalized SWCNT material in the form of bucky paper was mounted directly onto the holder with a clip, while powders were mounted directly onto carbon tape. The powders were pressed in a thick layer to insure that no carbon tape was exposed. The degree of functionalization (the ratio between functionalized and pristine sidewall carbons) was determined by a combination of XPS and TGA. TGA was used to calculate the degree of functionalization by calculating the ratio between the residual mass (attributed to pure SWCNTs) and the mass of the functional groups. XPS served as a complementary technique for determining the degree of functionalization. Since the composition of the functional group was known, a semi-quantitative estimate for the degree of functionalization can be made from the ratio of carbon to nitrogen in the sample. XPS gave an estimation of 3.4 % atomic percent of nitrogen, which compared to 3 % from TGA analysis.

A further XPS analysis, pictured in figure 4, aimed to examine the thermal stability and the decomposition temperatures of SWCNT-supported amine phases. Functionalized bucky papers were heated to temperatures of 200, 400 and 600 ºC and the nitrogen content for each of these samples were compared to that of a baseline material that was not heated. The nitrogen content remains relatively the same up to 200 ºC but begins diminish for above 200 ºC and is less than 0.1 atm % at 600 ºC. Thus XPS can assist in evaluating the thermal stability of functional groups on SWCNTs.

3.3 Platinum deposition

Because of their electrical conductivity, high surface areas, and stability under conditions of high temperature and pressure, various forms of carbon have been used as supports in proton exchange membrane fuel cells (PEMFC). Platinum metal is widely used as a catalyst in these PEMFC [39, 40] to augment the chemical reactions that produce electrons for power generation.

Platinum (Pt) metal can be incorporated in SWCNTs by depositing platinum from an acid solution onto high surface area supports followed by reduction of the platinum-bearing acid.

Electrodes were formed into buckypapers by vacuum filtration of SWCNTs dispersed in methanol. The buckypaper was impregnated with hexachloroplatinic acid dissolved in methanol that was subsequently allowed to evaporate, leaving behind hexachloroplatinic acid residue. The impregnated buckypaper was then heated to 700 ºC in an inert atmosphere to reduce the platinum. Electrodes were analyzed by XPS to determine the chemical state of platinum as well as a relative measure of the amount of platinum deposited in the electrode.

In order to determine the concentration of platinum deposited onto the electrode a large beam size and pass energy where used to maximize the analysis area and signal. The sample was sputtered for 10 minutes so that surface contaminants on the Pt would not contribute to an underestimation of the Pt concentration (see figure 5), which was determined to be 1 atm. %. In order to determine the chemical environment of the platinum, decreasing the pass energy, while maintaining the spot size, increased the energy resolution of the analyzer. This analysis was performed over several locations within the sample surface. The sample was analyzed before and after sputtering to determine whether a native oxide on the Pt existed or whether this was a bulk oxide. This is important for fuel cell applications since an oxide film will reduce the catalytic property of Pt. The Pt 4f peaks were used to determine the platinum chemical state. The results suggest that our Pt deposition process incorporates the Pt in a reduced state and not as an oxide or chloride of Pt. XPS was thus capable of providing information on the relative concentration as well as the chemical state of the Pt deposited into SWCNT material.

Conclusions:

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A protocol for characterizing carbon nanotube materials by XPS has been developed that takes into consideration all of the factors that can influence the XPS data of carbon nanotubes. This protocol is a suggestive guideline to aid in maximizing the results obtained from XPS and variables should be selected in accordance to particular characterization needs. This protocol could conceivably be extended to both Auger and ultra-violet photoelectron spectroscopy.

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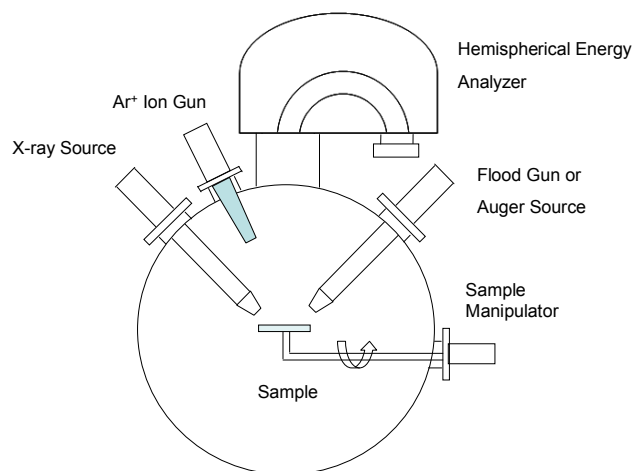
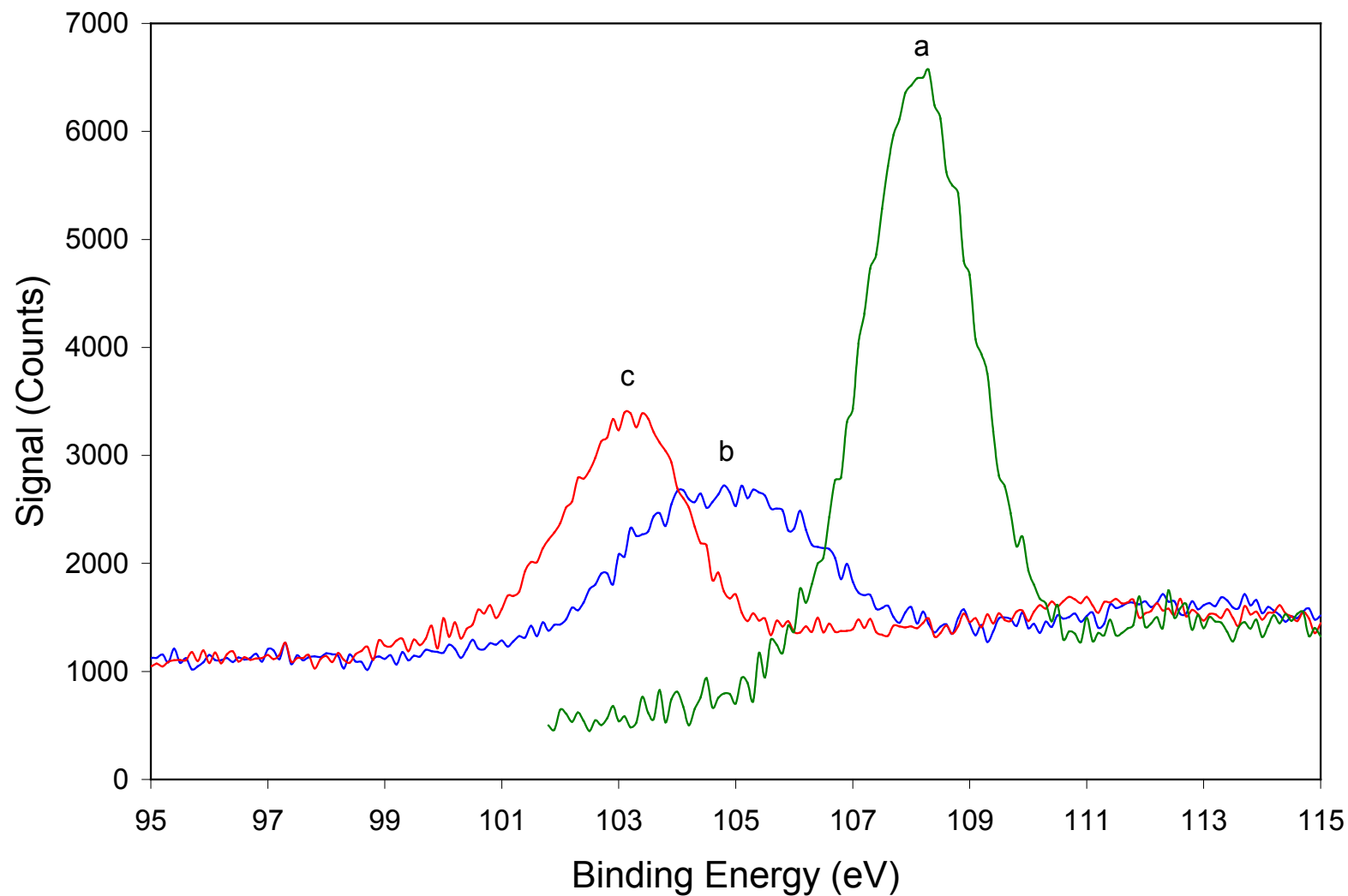Figure 1. Schematic of an XPS system showing the major components.

Figure 2. The effect of surface charging on the SiO_2 peak within as produced SWCNTs residual ash from samples with a) no coating or neutralizer gun, b) coated with AuPd but no neutralizer gun, c) coated and the use of a neutralizer gun. Spectra (b) and (c) were taken with monochromatic Al source while a spectrum (a) was taken with a dual anode source.
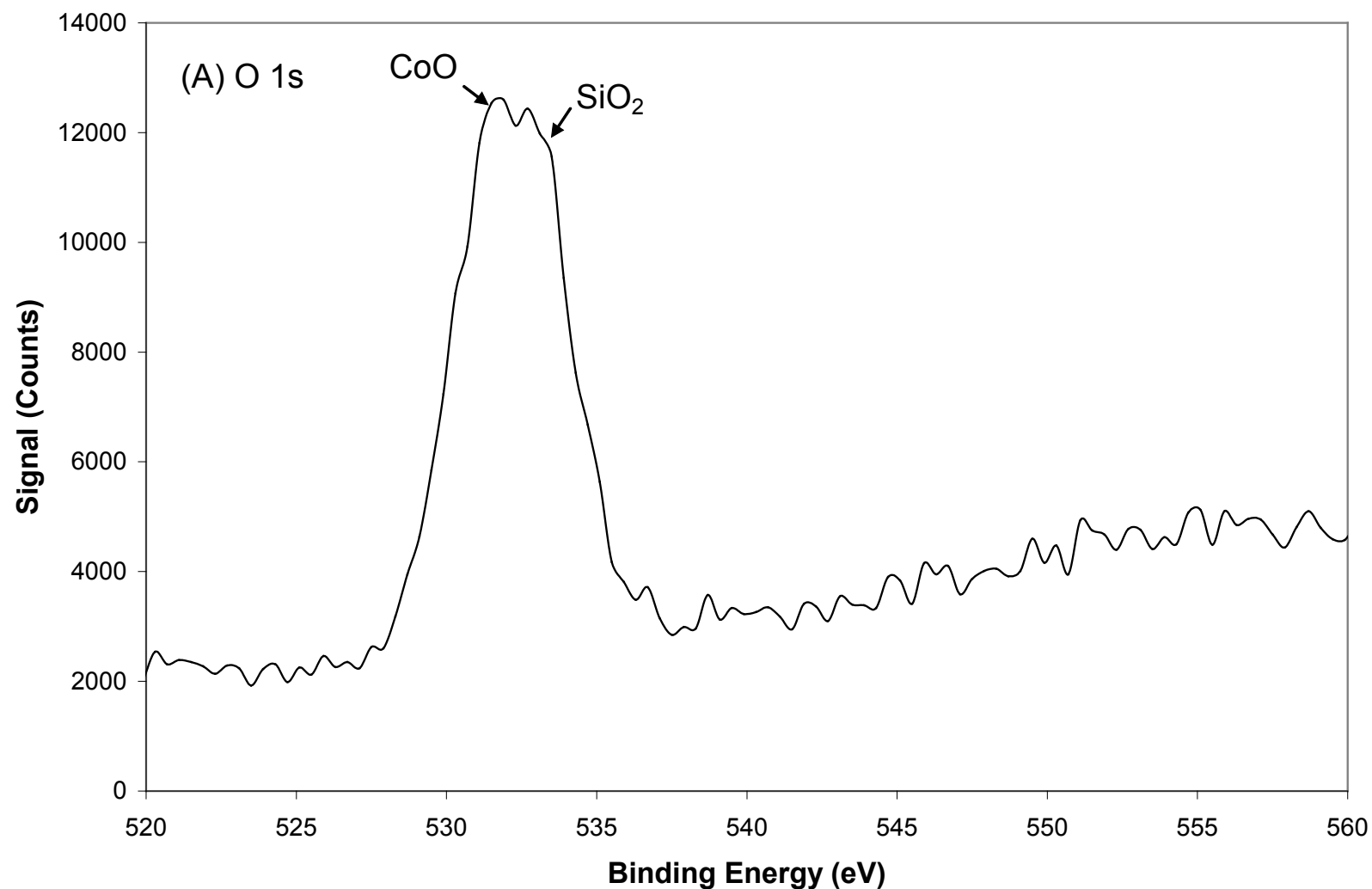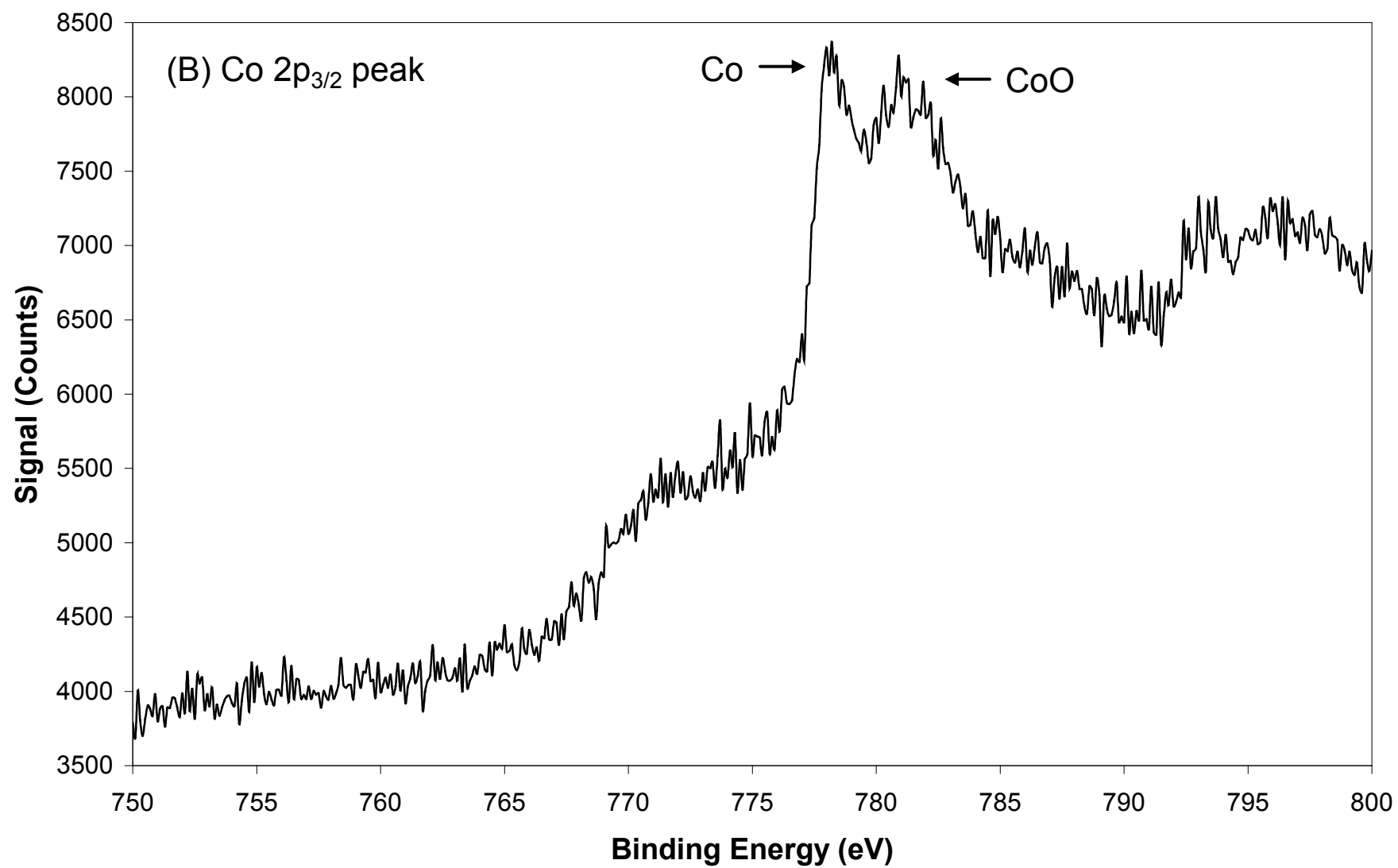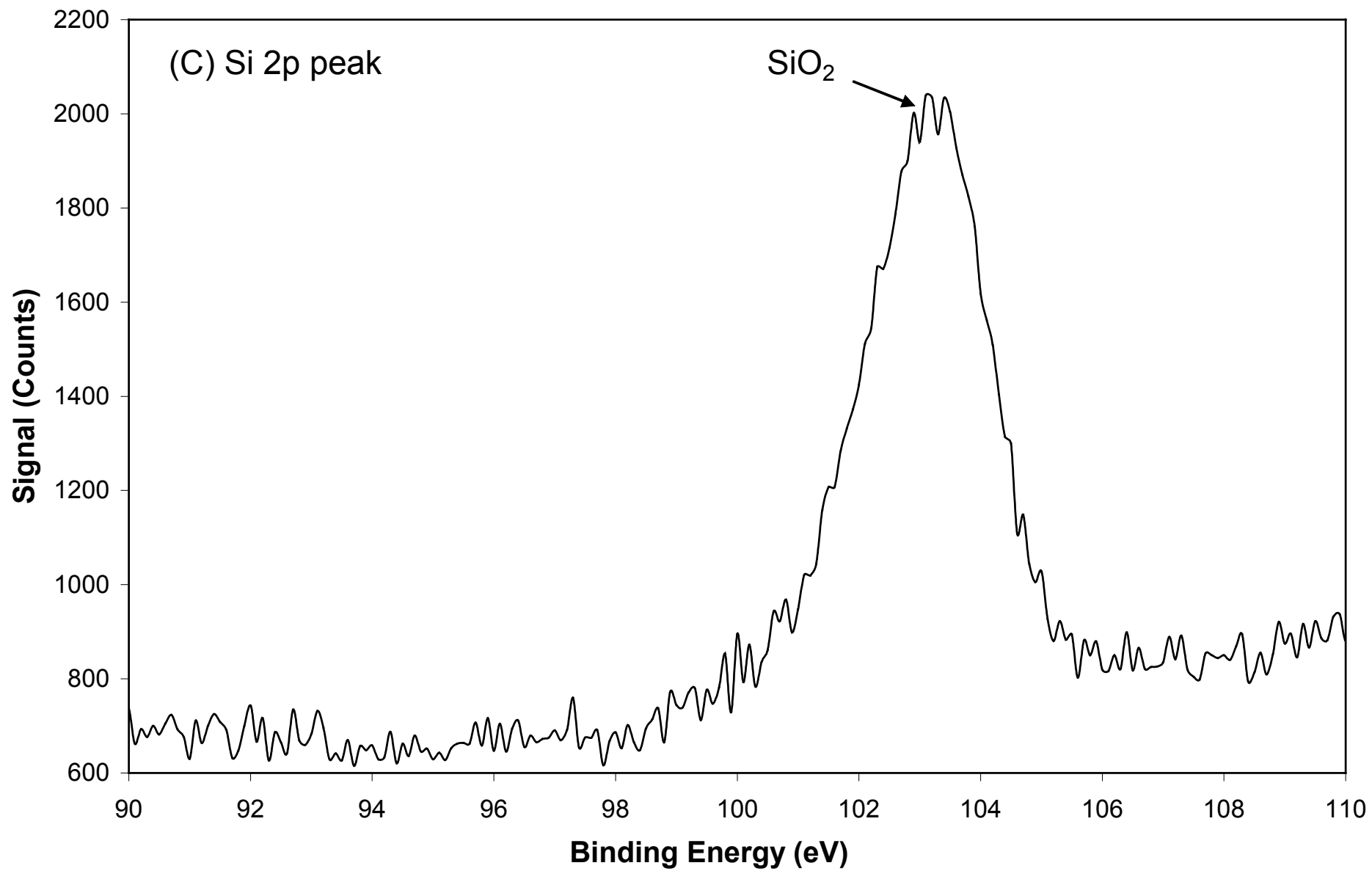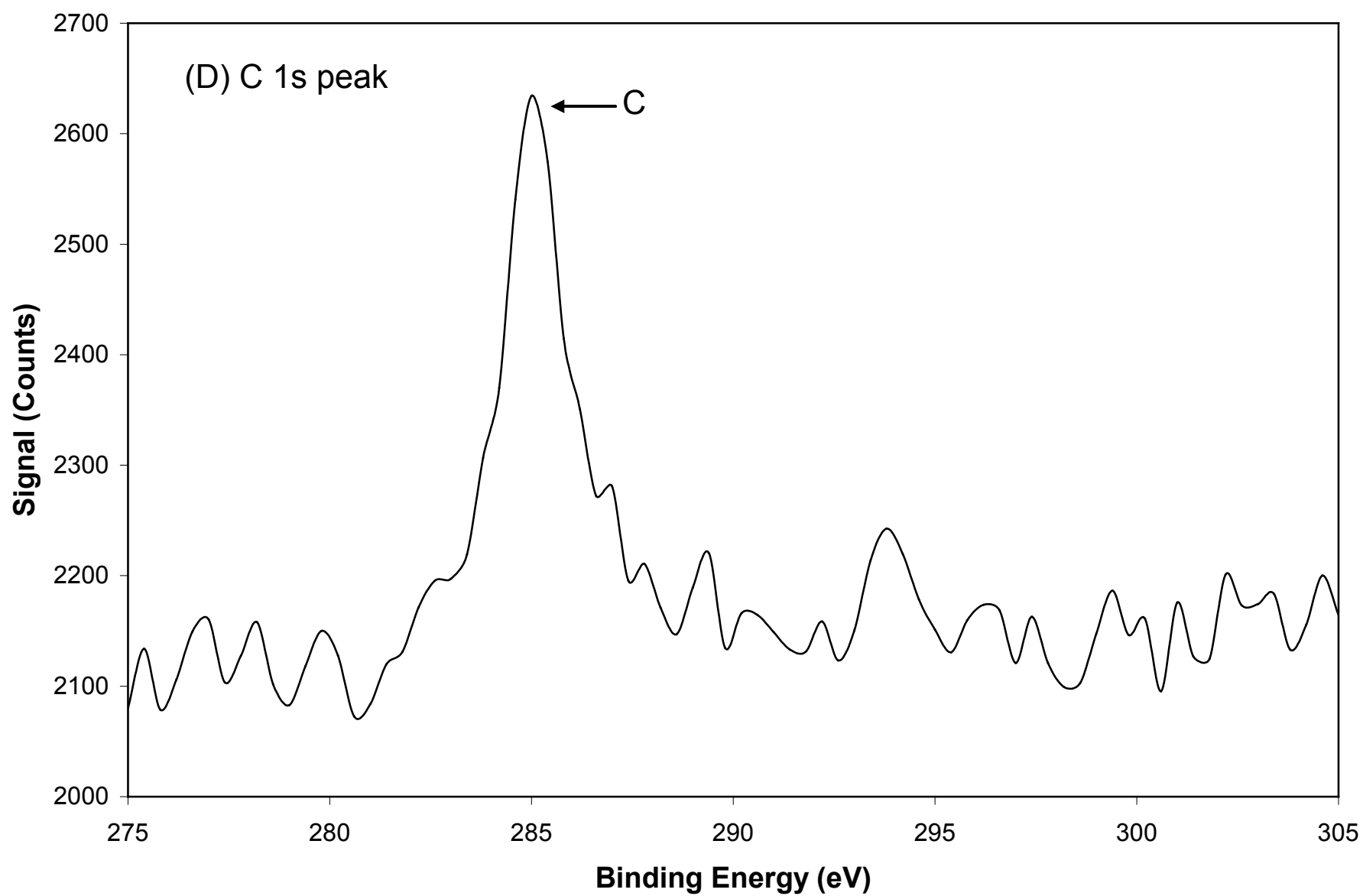
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Figure 3. XPS spectra of the TGA residual ash constituents (A) O, (B) Co, (C) Si, (D) C, (E) Ni, from laser produced SWCNTs. Silicon (B.E.=103.1eV) in ash is present as SiO_2 with the small shoulder on the low energy side attributed to Co and not to SiC which is confirmed by the position of the C 1s peak. The Co is partially oxidized while the nickel in the residual ash is in reduced form. The oxygen peak taken from the survey scan identifies two species which are attributed to CoO and SiO_2 oxygen. Spectra for Co, Ni and Si were taken with a pass energy of 55eV (0.33eV resolution) while C and O were taken with a pass energy of 112 eV (0.67eV resolution).

(B) Co 2p$_{3/2}$ peak

Co → ← CoO

Signal (Counts) vs Binding Energy (eV)

(C) Si 2p peak

SiO$_2$

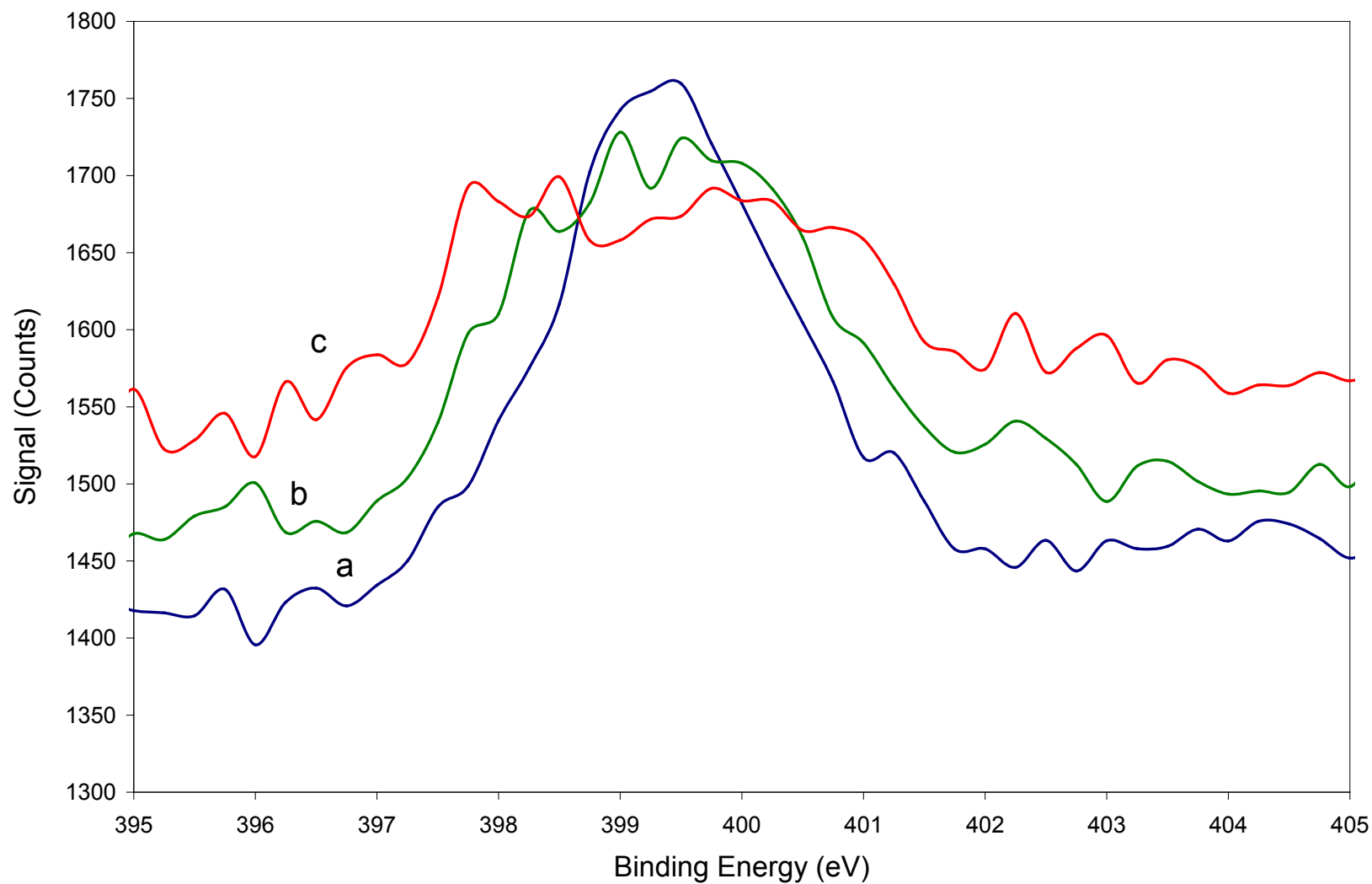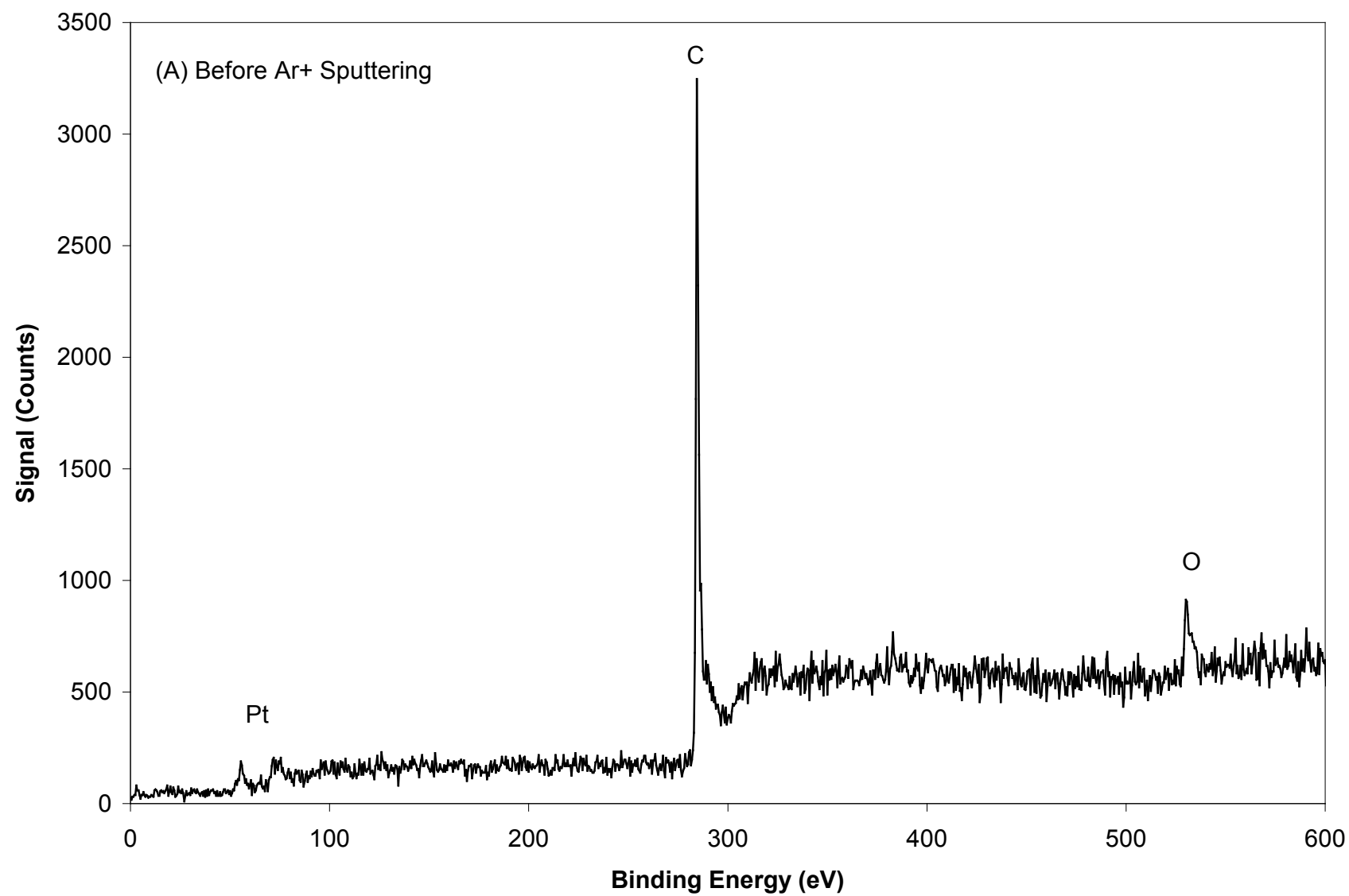(D) C 1s peak

(E) Ni 2p$_{3/2}$ peak

Ni
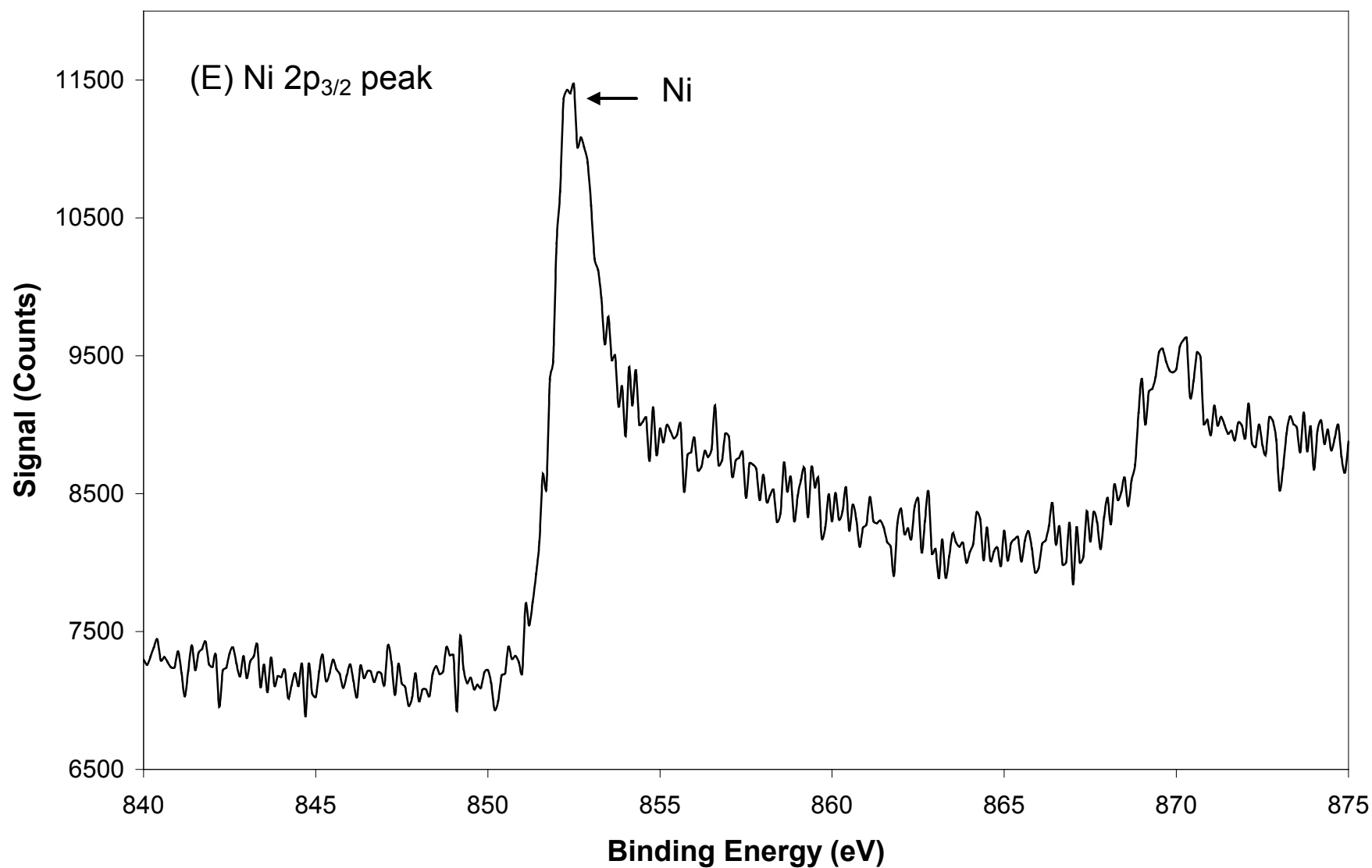
Figure 4. The nitrogen content of each sample can be viewed by the reduction in the height of the N1s peak for the XPS spectra taken after ex-situ heating of the sample to (a) 200 C, (b) 400 C and (c) 600 C. The vertical shifting of the peaks can be attributed to backscattering of electrons.
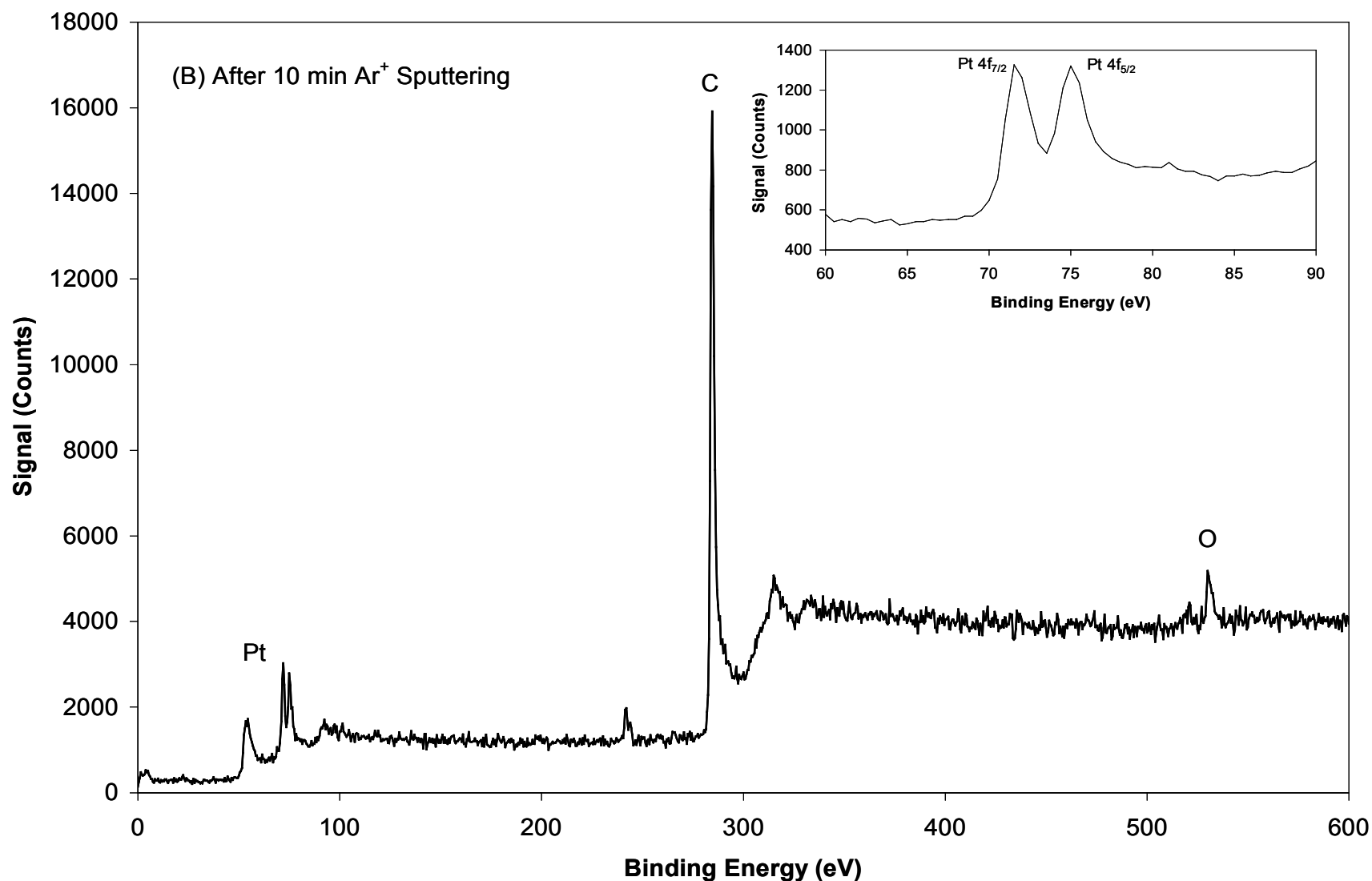
(A) Before Ar+ Sputtering

Figure 5. XPS of a SWCNTs fuel cell membrane impregnated with Pt particles before (A) Ar^{+} sputtering and (B) after 10 minute Ar^{+} sputtering. Inset shows the Pt 4F peaks which have energies corresponding to metallic platinum. Oxygen present is attributed to residue from ethanol used in sample preparation.