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Surface chemical analysis — Characterization of nanostructured materials

Analyse chimique des surfaces - Caractérisation des matériaux nanostructurés

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

This second edition cancels and replaces the first edition (ISO/TR 14187:2011), which has been technically revised.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

As engineered nanomaterials of many types play an increasing role in many different technologies[1], international organizations (including ISO, ASTM, the International Bureau of Weights of Measures (BIPM), Consultative Committee for Amount of Substance: Metrology in Chemistry (CCQM) and the Organization for Economic Cooperation and Development (OECD))[1] are working to identify critical properties[2] and measurements that must be understood to adequately and reproducibly define the nature of the materials being used.

A large percentage of any nanomaterial is associated with a surface or interface. Therefore, surface composition and chemistry have been identified as being part of a minimum set of chemical parameters needed to characterize nanomaterials and it would naturally seem that the wide range of tools developed for surface characterization could or should be routinely applied to these materials. Two different issues, however, have limited the impact of traditional surface analysis tools in some areas of nanoscience and nanotechnology. First, many of the tools do not have sufficient spatial resolution in three dimensions needed to analyse individual nanostructured materials (or, equivalently, variations of composition within that material). For this reason, some researchers do not consider application of the tools even though they can often provide very important information. Second, surface analytical (and other) tools are often applied to nanostructured materials without appropriately considering several analytical challenges or issues that these materials present. Such challenges include environmentally altered behaviours of nanoparticles (including effects of making measurements in vacuum), time-dependent characteristics of nanostructured materials, the influence of particle shape on analysis results, and the increased possibility of altering the structure or composition of the nanomaterial by the incident radiation (typically electrons, X-rays, or ions) during the analysis.

As noted by others including Linkov et al.[3] there are new challenges associated with understanding and characterizing nanomaterials, “the study of nanostructures and nanomaterials requires special protocols that take into account the physical [and chemical] phenomena that occur in nanosized systems.” This document gives information on these important issues. The report first describes the types of information that can be obtained about nanostructured materials, sometimes using analytical approaches beyond those in standard applications. Second, the report examines the technical challenges generally faced when applying surface analysis tools (and often other tools) for characterization of nanostructured materials as well as those specific to each technique.

Because of the expanding use of nanostructured materials in research, development, and commercial applications as well as their natural presence in air, surface, and ground water, there is an increasing need to understand the properties and behaviours of nanostructured materials as they are synthesized or as they evolve in a particular environment. The novel and unusual properties of nanostructured materials excite scientists, technologists and the general public. However, the sometimes surprising properties of many of these materials raise reproducibility, analysis or characterization issues that sometimes are unexpected by analysts, scientists, and production engineers[4-6]. There is an increasing awareness of reproducibility issues in many areas of science including those associated with materials, biological, computational, and chemical research[7-11]. Inherent characteristics of nanoparticles (NPs) that make them interesting and potentially useful also make them susceptible to reproducibility challenges associated with their production, characterization, and delivery. Inconsistencies and conflicts caused by these challenges have stimulated editorials and commentaries[5-12], scientific news items, and journal articles[4,15-18]. Careful analysis, including surface analysis as described in this report, along with data records such as described in ISO 20579-4 for preparation of nano-objects for surface analysis can help establish the provenance of a batch of nano-objects[19,20] providing a tool to address nano-object reproducibility issues.

Potential health and environmental concerns related to materials with unusual or unique properties increase the need to understand the chemical, physical and biological properties of these materials throughout their life cycle. It is now recognized that some early reports on the properties of nanoparticles and other nanostructured materials, including their toxicity and environmental stability, were based on inadequate characterizations[13]. In some cases, important characterizations appear not to have been attempted or reported[21,22]. A March 2006 article in Small Times magazine described a workshop designed to identify roadblocks to nanobiotech commercialization[13] at which several experts reported that many of the important physical characteristics needed to understand the physical and chemical properties of nanoparticles were not reported and apparently often unmeasured, especially in assessments of particle toxicity. The article further notes that the changes that these particles undergo when exposed to the environment where they are stored or used are especially important and usually unknown. In many cases, nanoparticles are coated with surfactants or contaminants, and these are often not well characterized and sometimes not adequately identified. As a result, the validity of the conclusions may be questionable. Inadequate characterization of the surface chemistry of nanoparticles has been identified as one of the areas where appropriate characterization is often lacking[5,22]. This issue was identified also by the OECD Working Party on Manufactured Nanomaterials (WPMN) and new projects are launched under the umbrella of the Malta Initiative. One of them is the "Identification and quantification of the surface chemistry and coatings on nano- and microscale materials" where surface chemical analysis will substantially contribute.

The ISO definition of a nano-object (ISO/TS 80004-1:2015) is that, in at least one dimension, the size of the object or structure must be approximately 100 nm or less. Considerable attention is being given to the characterization of nanosized-objects (particles, rods or other shapes) that might be released into the environment and a set of minimum characterization requirements for nanoparticles for use in toxicity studies has been identified[2]. However, the needs for nanomaterials characterization include the wide variety of nanostructured materials that are used in computers, as sensors, in batteries or fuel cells and many other types of applications. Nonetheless, the minimum characterization requirements for nanoparticles can be generalized to a wider range of materials and potential applications as shown in Table 1.

Surface-analysis methods of various forms (described later) can provide information that relates to many elements in Table 1 including those that appear obvious (such as surface composition and chemistry) but also includes particle or component size, presence of surface impurities, nature of surface functionality (including acidity), surface structure/morphology, near-surface variation of composition (both laterally and with depth, coating/film thickness, and electronic properties of nanostructures/films.

Surface characterization is only a subset of several nanomaterials analysis needs that are being examined by ISO/TC 229. This report on surface chemical analysis methods prepared by ISO/TC 201/SC 7 has been prepared in coordination with the overall characterization needs identified by experts in TC 201 and TC 229 as well as awareness of the objectives being addressed by ISO/TC 229. This document describes the information that can be obtained (and by which techniques), and examines some of the issues and challenges faced when performing such analyses.

Table 1 — Physical and chemical properties for characterization of nanostructured materials

*Items in **bold** font are properties for which surface chemical analysis can provide useful information, as described in this document.*

What does the material look like?

- **Particle/grain/film/structural unit size**(s) /size distribution
- **Grain, particle, film morphology** (shape, layered, roughness, topography)
- Agglomeration state/aggregation (e.g., do particles stick together)

What is the material made of?

- Bulk composition (including chemical composition and crystal structure)
- Bulk purity (including levels of impurities)
- **Elemental, chemical and/or phase distribution** (including surface composition and surface impurities)

What factors affect how a material interacts with its surroundings?

- Surface area
- **Surface chemistry**, including reactivity, hydrophobicity
- Surface charge

Overarching considerations to take into account when characterizing engineered nanomaterials (for toxicity studies and other applications):

- **Stability**—how do material properties (especially the surface composition, particle agglomeration, etc.) change with time (dynamic stability), storage, handling, preparation, delivery, etc.? Include solubility and the rate of material release through dissolution
- Context/media—how do material properties change in different media or during processing (**environmental effects**); i.e., from the bulk material to dispersions to material in various biological matrices? ("as administered" characterization is considered to be particularly important)
- Where possible, materials should be characterized sufficiently to interpret **functional behaviours**. For toxicology studies, information is required on the response to the amount of material against a range of potentially relevant dose metrics, including mass, surface area, and number concentration

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This table is adapted from [2]. The recommendations in the initial table were developed at a workshop on ensuring appropriate material characterization in nanotoxicology studies, held at the Woodrow Wilson International Center for Scholars in Washington, DC, USA, between 28 October and 29 October, 2008; http://www.characterizationmatters.org.

Surface chemical analysis — Characterization of nanostructured materials

1 Scope

This document provides an introduction to (and some examples of) the types of information that can be obtained about nanostructured materials using surface-analysis tools (Clause 5). Of equal importance, both general issues or challenges associated with characterizing nanostructured materials and the specific opportunities or challenges associated with individual methods are identified (Clause 6). As the size of objects or components of materials approaches a few nanometres, the distinctions among “bulk”, “surface” and “particle” analysis blur. Although some general issues relevant to characterization of nanostructured materials are identified, this document focuses on issues specifically relevant to surface chemical analysis of nanostructured materials. A variety of analytical and characterization methods will be mentioned, but this report focuses on methods that are in the domain of ISO/TC 201 including Auger Electron Spectroscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and scanning probe microscopy. Some types of measurements of nanoparticle surface properties such as surface potential that are often made in a solution are not discussed in this Report.

Although they have many similar aspects, characterization of nanometre-thick films or a uniform collection of nanometre-sized particles present different characterization challenges. Examples of methods applicable to both thin films and to particles or nano-sized objects are presented. Properties that can be determined include: the presence of contamination, the thickness of coatings, and the chemical nature of the surface before and after processing. In addition to identifying the types of information that can be obtained, the document summarizes general and technique-specific Issues that must be considered before or during analysis. These include: identification of needed information, stability and probe effects, environmental effects, specimen-handling issues, and data interpretation.

Surface characterization is an important subset of several analysis needs for nanostructured materials. The broader characterization needs for nanomaterials are within the scope of ISO/TC 229 and this document has been coordinated with experts of TC 229 Joint Working Group (JWG) 3.

This introduction to information available about nanomaterials using a specific set of surface-analysis methods cannot by its very nature be fully complete. However, important opportunities, concepts and issues have been identified and many references provided to allow the topics to be examined in greater depth as required.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 18115-1, *Surface chemical analysis — Vocabulary — Part 1: General terms and terms used in spectroscopy*

ISO 18115-2, *Surface chemical analysis — Vocabulary — Part 2: Terms used in scanning-probe microscopy*

3 Terms, definitions and abbreviated terms

For the purposes of this document, the terms and definitions given in ISO 18115-1 and ISO 18115-2 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

Symbols and abbreviated terms

AES	Auger electron spectroscopy
APT	atom probe tomography
AFM	atomic force microscopy
ARXPS	angle resolved X-ray photoelectron spectroscopy
CNT	carbon nanotube
CVD	chemical vapour deposition
dSIMS	dynamic secondary ion mass spectrometry
EI-MS	electron ionization mass spectrometry
EPMA	electron probe micro-analysis
ESCA	electron spectroscopy for chemical analysis (same as XPS)
G-SIMS	gentle secondary ion mass spectrometry (a variant of SIMS to extract information about molecular groups)
HRLEIS	high resolution - low energy ion scattering
ICP-MS	inductively coupled plasma mass spectrometry
IMFP	inelastic mean free path
IRS	Infrared Spectroscopy
ISS	ion scattering spectroscopy
LED	light emitting diode
LEIS	low energy ion scattering
LRS	laser Raman spectroscopy
MultiQuant	spectrum evaluation program for quantitative evaluation of XPS data
MWCNT	multi-walled carbon nanotube
NRA	nuclear reaction analysis
PECVD	plasma enhanced chemical vapour deposition
PEM fuel cell	polymer electrolyte membrane fuel cell
PMMA	poly(methyl methacrylate),
PPV	poly(diakloxy-p-phenylene vinylene)
PVB	poly(vinyl butyral)
QUASES	quantitative analysis of surfaces by electron spectroscopy (computer program for quantitative evaluation of XPS and Auger spectra)

RBS	Rutherford backscattering spectroscopy
SEM	scanning electron microscopy
SESSA	simulation of electron spectra for surface analysis (computer program for quantitative evaluation of XPS and AES spectra)
SHG/SFG	second harmonic generation/sum frequency generation
SI	secondary ion
SIMS	secondary ion mass spectrometry
SNOM	scanning near-field optical microscopy
SPM	scanning probe microscopy (a generic term covering STM, AFM and other scanning tip-based microscopies)
sSIMS	static secondary ion mass spectrometry
STM	scanning tunnelling microscopy
SWCNT	single walled carbon nanotube
TEM-PEELS	transmission electron microscopy - parallel electron energy loss spectroscopy
TCNQ	tetracyanoquinodimethane
TOF-SIMS	time of flight – secondary ion mass spectrometry
WPMN-OECD	Working Party on Manufactured Nanomaterials – Organization for Economic Co-operation and Development
XPS	X-ray photoelectron spectroscopy
μTA	microthermal analysis

4 Characterization of nanostructured materials with surface analysis methods

4.1 Introduction

Surfaces and interfaces can strongly influence many properties of materials and material systems. Surfaces control chemical reactivity, influence adhesion, and are associated with heat and electron transfer. In many circumstances, the surface composition may differ from the bulk composition due to surface contamination or to segregation (enrichment) of one component. Interfaces between grains of one material or of differing materials are critical to the performance of electronic materials and the strength of structural materials. Because of the importance of surfaces and interfaces, special tools have been developed to determine their compositions and to assess how these affect the properties of natural and engineered materials. Significant groupings of surface analysis tools include those based on electron spectroscopy (Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS)), those involving incident ion beams (secondary ion mass spectrometry (SIMS) and low-energy ion scattering (LEIS), and those based on scanning probe microscopy (SPM) including atomic force microscopy (AFM) and scanning tunnelling microscopy (STM). These tools are widely applied to characterize natural and engineered surfaces in relation to fundamental studies, for material and product development, and for analysing product reliability and performance in service environments. These analysis methods have provided significant value in many technologies including pharmacology, health, microelectronics, chemical, power, transport and aerospace, and the advanced materials used in many technologies.

Although other surface-analysis techniques are used and will be mentioned in this report, the focus will be on AES, LEIS, SIMS, SPM, and XPS and the application of these techniques to the characterization of nanostructured materials; it is noted that there are subcommittees for all of these methods except LEIS within ISO/TC 201. Detailed discussions of these methods are available from many sources[23,24]. Information on the typical spatial resolutions of AES, SIMS, SPM, and XPS is summarized in Figure 1. In all cases, the techniques have nanometre resolution in at least one dimension.

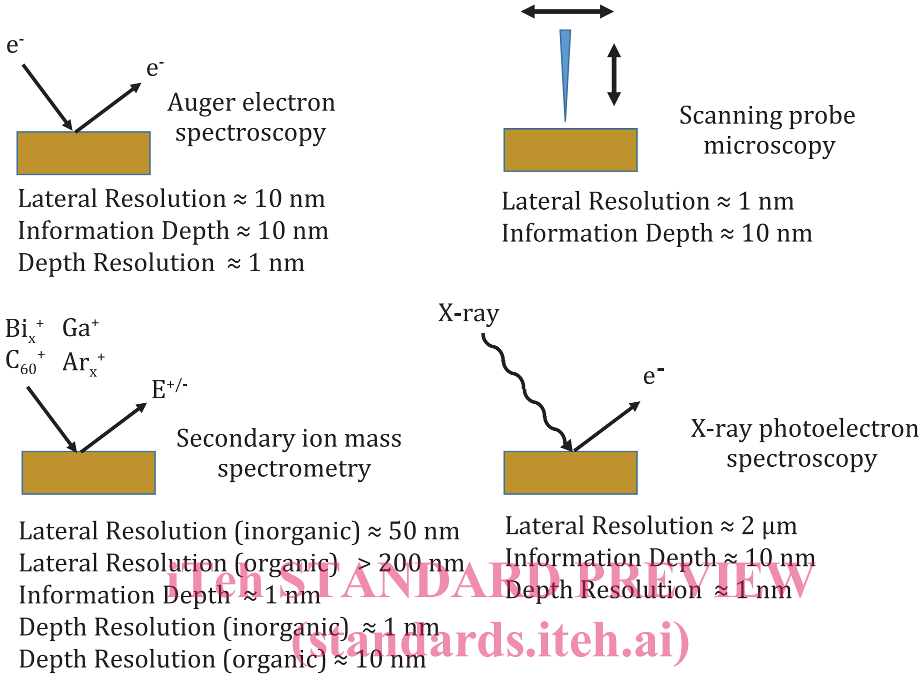

Figure 1 — Schematic overview of probing and detected species for surface analysis by AES, SIMS, SPM, and XPS (also indicated are the typical spatial resolutions available with these surface-analysis methods)

In addition to having differences in spatial resolution, different surface analysis techniques can provide different types of information. The UK National Physical Laboratory[25] has created a drawing that summarizes the types of information that can be provided by many different analysis methods, as shown in Figure 2. The types of information that can be obtained include topography, elemental composition, molecular and chemical state, and structural information. Useful or potentially useful methods not included in Figure 2 include LEIS, laser Raman spectroscopy, and nonlinear optical methods such as second harmonic generation (SHG) and sum frequency generation (SFG). LEIS has also been known as Ion Scattering Spectrometry (ISS) and is a well-established method. However, in modern instruments it can be particularly useful because of the high sensitivity to the very outermost atomic layers of a sample[26]. A few examples of LEIS will be included in the examples provided in later sections. TOF-SIMS is often applied in the static mode and is indicated by Static SIMS in Figure 2. Full chemical structure would include information about the molecular structure of the elements and molecules present in the sample or on the sample surface. Several methods provide some, but not comprehensive, information about molecular structure.

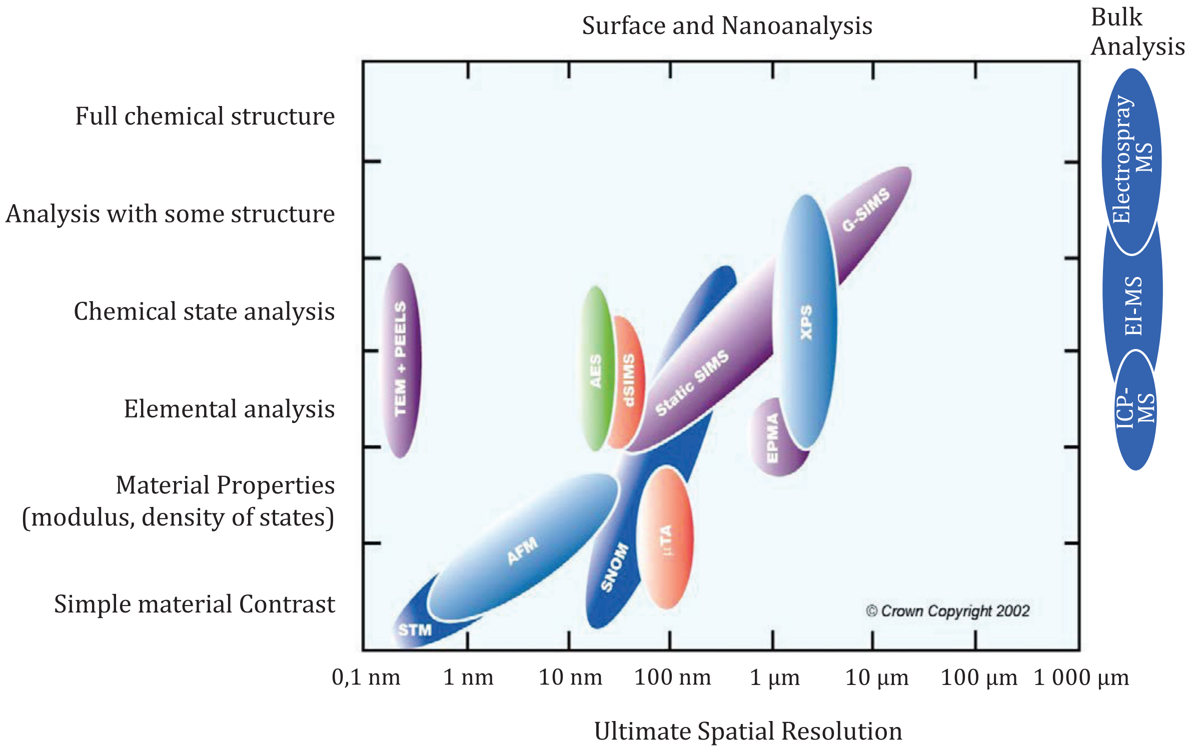

Figure 2 — Diagram providing overview of spatial resolution and types of information that can be ordained by a range of tools important for the analysis of nanostructured materials[25]

It has already been noted that nanostructured materials inherently involve a high percentage of atoms located on or near surfaces or interfaces, and that the material properties are significantly impacted by the nature and properties of these surfaces and interfaces in addition to any fundamental changes in materials properties due to their overall small size. Among the materials properties that must be known to understand behaviour are characteristics related to surface chemistry and surface charge. Specific knowledge is often required on the presence and properties of surface layers and surface contamination, the chemical state or enrichment of species on the surface or at interfaces, and information about surface functionality. Examples of the types of information needs and techniques by which they can be addressed are shown in Table 2. Table 2 includes commonly used tools beyond those shown in Figure 1 but is not intended to be comprehensive.

Although many analysis tools can be useful for characterizing nanostructured materials, it is important to recognize that there are many challenges and unmet analysis needs for such applications. Some challenges are associated with limitations of the current tools[6,27] or with challenges in using (or having access to) all of the needed tool set[4,5], Issues associated with environmentally induced changes, damage or sample handling issues[3,28], will be discussed in Clause 6.

Table 2 — Information needs and relevant tools for nanostructured material surfaces

Type of Information	Film or nanoparticle	Possible Techniques	Comments or range of applicability
Surface composition (including surface functionalization)	Nanometre films	XPS, AES	Outer 10 nm
		LEIS	Outer <1nm
		SIMS	Outer 1 nm
	Nanoparticles	XPS, AES, SIMS, LEIS	As above

Table 2 *(continued)*

Type of Information	Film or nanoparticle	Possible Techniques	Comments or range of applicability
Depth distribution	Nanometre films	XPS RBS, NRA Atom Probe Tomography Sputter profiles using AES, XPS, SIMS	Outer 10 nm non-destructively About 2 µm up to 1 µm Less than ~1 µm
	Nanoparticles	XPS, AES, TEM, APT	
Layer thickness	Nanometre Films	XRR, SPS, RBS, Ellipsometry, AES	
	Nanoparticles	AES, XPS, TEM	
Molecular structure	Nanometre films	Raman/IRS TOF-SIMS	
	Nanoparticles	Raman/IRS TOF-SIMS	
Surface roughness	Nanometre films	AFM, Profilometry	
	Nanoparticles	TEM, AFM, SEM	
Size	Nanoparticles	TEM, SEM, AFM, XPS	

In the following three subclauses, five surface-analysis methods (AES, XPS, LEIS, SIMS, and SPM) are briefly described and examples of their use for nanomaterials characterization are given. The examples indicate what can be done but do not provide a comprehensive picture. To highlight some differences and similarities in analytical approaches, examples of characterization of nanostructured thin films and nanoparticles will be provided. In addition to these examples, a separate section will discuss characterization of carbon nanotubes (CNTs). Applications are often limited only by the ingenuity of the research team involved. It will also be apparent that these tools are generally most useful when they are applied in combination with other techniques that provide complementary information (**multi-technique analysis**). Such complementary information is often essential for characterizing the samples and may also alert analysts to environmental or probe-initiated effects (sample damage) that alter the material or confuse the results. Care is also required for sample handling and preparation of samples for analysis without introducing sample changes or contamination[28-30].

4.2 Electron Spectroscopies (AES and XPS)

Both AES and XPS can detect the presence of all elements with the exception of H and He and involve the detection of electrons emitted from samples with kinetic energies typically below 2 000 eV. Much of the value of these methods is their surface sensitivity that arises from the short distances that electrons travel at these energies without undergoing inelastic scattering and energy loss[31-33]. Therefore the electrons detected in Auger or photoelectron peaks are from the outer few nanometres of the material, as indicated in Figure 2. Catalysis was one of the first areas where the combination of “bulk” analysis methods with these surface analysis methods allowed information about the enrichment or depletion of elements on the surface to be determined[34-36]. Because electrons that emerge from the material and have lost energy appear in the background region of the spectra[37], it is possible to use these methods to provide depth, enrichment or layering information within the XPS and AES analysis volume. Consequently, these two methods can be used with multiple approaches to obtain important information about layering or coatings on films, particles and nanoparticle surfaces[38].

Although both X-ray and electron excitations produce Auger electrons, AES is usually associated with incident-electrons during which Auger electrons are produced. These incident electrons typically range in energy from 2 keV to as much as 25 keV. X-rays (often Mg or Al Kα) are typically the incident radiation in XPS, which was initially called Electron Spectroscopy for Chemical Analysis (ESCA) by Kai Siegbahn who was awarded a Nobel Prize in Physics for his development of this technique. Because an electron beam can be focused to tens of nanometres in size, it is possible to analyse individual nanoparticles with AES. However, issues related to electron penetration and scattering can cause significantly worse resolution than expected[25] based on beam size alone. Although XPS does not have the spatial resolution to analyse individual nanoparticles (with the possible exception of a few special synchrotron-based systems with highly focused X-ray beams or photoelectron-imaging systems), it is often possible to analyse collections of particles (in a single layer or effectively in powder form) and to obtain useful information[31,38,40].

Both AES and XPS can be extremely important tools for determining the presence, composition and thickness of coatings on films and nanoparticles as well as surface enrichment and depletion at surfaces. To the surprise of many, XPS can sometimes be used to determine particle sizes when conditions are not appropriate for analysis by other methods[31,36,41]. The size, shape, and layered structure of nanostructured materials influence XPS data in several different ways including:

- Peak intensities and relative peak intensities of
  - peaks for different elements
  - different peaks for the same element
- Peak energies
  - binding energies of peaks
  - values of the Auger parameter
- Background signals from electrons that have lost energy

These effects are more fully described in the literature[31,42] and on the web[41]. Depending on what is known about the specimen and the objectives of the analysis, each of these effects can be used to extract useful information about nanostructured samples including:

i) Verification of surface functionalization and product formation

ii) Presence of contamination, coatings, and oxidation

iii) Orientation of surface molecules

iv) Surface enrichment or depletion

v) Layer thickness

vi) Particle size and particle location

vii) Other Properties: Electronic characteristics of thin films and particles, and surface acidity.

Many different research teams have used AES and XPS to characterize a wide variety of nanostructured materials. Many of them have focused on surface films or nanolayers, while others have focused on nanoparticles of various types. A few examples highlight the role of XPS in some studies. Other applications are simply listed to show the range of research areas where XPS and AES have been used.

4.2.1 Surface functionalization and product formation - Perhaps the most common uses of XPS for characterization of nanostructured materials involve confirmation of the reactions expected to occur during synthesis or the presence of functional groups on a surface. These types of experiments take advantage of the surface sensitivity and chemical-state information available from XPS. For confirmation of the addition of a type of surface species or confirmation of product formation only a simple analysis may be required. These are sometimes highly important experiments that involve relatively straightforward XPS measurements.

For example, in a set of clever experiments by Lim and co-workers[43], D and L cysteines were attached to the surfaces of Au nanoparticles and used to regulate interparticle chiral recognition. For these studies, XPS was used to confirm the presence of the cysteines and to demonstrate the consistent nature of the surface coverage and binding of the different types of cysteines to the nanoparticle surfaces. An import