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Surface chemical analysis — Characterization of nanostructured materials

Analyse chimique des surfaces — Caractérisation des matériaux nanostructurés

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Foreword

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In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

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ISO/TR 14187 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 5, *Auger electron spectroscopy*.

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 define the nature of the materials being used. An inherent property of any nanostructured material, whether a particle, fibre or other object, is that a large percentage of the material 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 need 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. This Technical Report 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 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 analysis or characterization issues that sometimes are unexpected by analysts, scientists, and production engineers [3-5].

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 [6]. In some cases, important characterizations appear not to have been attempted or reported [7, 8]. A March 2006 article in Small Times magazine described a workshop designed to identify roadblocks to nanobiotech commercialization [6] 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 [4, 8]. One of the definitions of a nanostructured material is that, in at last one dimension, the size of the object or structure must be 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 5 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 Technical Report 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 Technical Report.*

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

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 Technical Report provides an introduction to (and some examples of) the types of information that can be obtained about nanostructured materials using surface-analysis tools (Section 4). 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 (Section 5). 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 Technical Report 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 Technical Report 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 report 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 Terms and definitions

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

3 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	a 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 anlaysis

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 [9, 10]. 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.

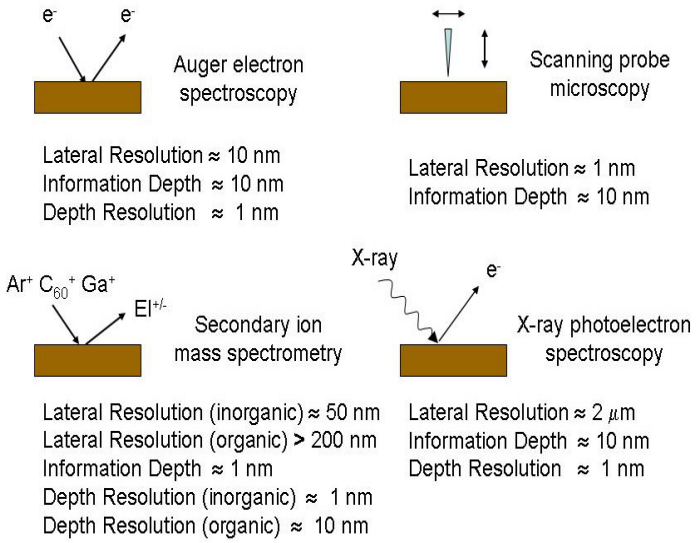


Figure 1. Schematic overview of probing and detected species for surface analysis by AES, SIMS, SPM, and XPS. Also indicated are the typical spatial resolutions available with these surface-analysis methods.

In addition to having differences in spatial resolution, different surface analysis techniques can provide different types of information. The UK National Physical Laboratory [11] 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 Fig. 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 [12]. 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.

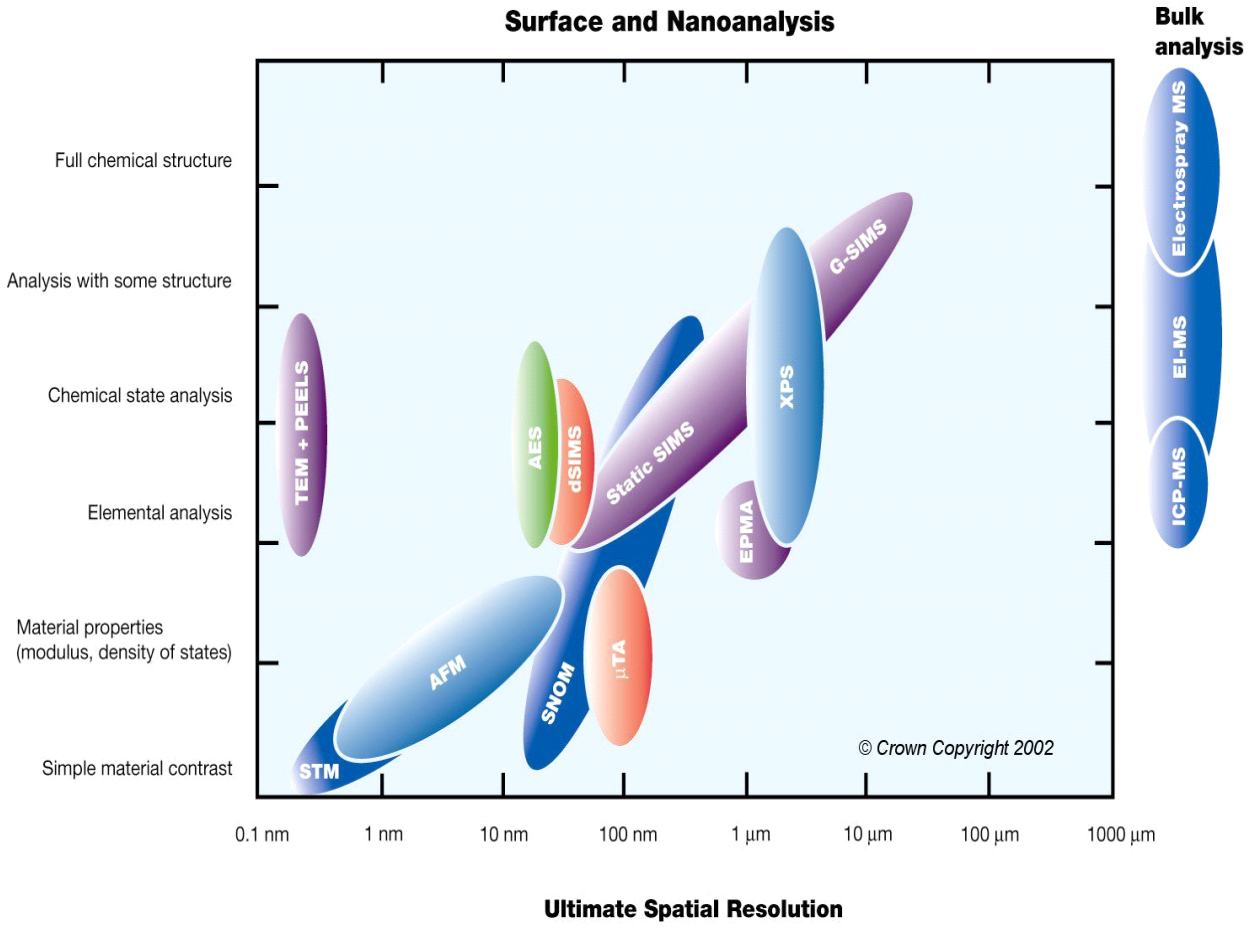


Figure 2. Diagram providing overview of spatial resolution and types of information that can be ordained by a range of tools important for the analysis of nanostructured materials. After reference [11].

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 [5, 13] or with challenges in using (or having access to) all of the needed tool set [3, 4], Issues associated with environmentally induced changes, damage or sample handling issues [3, 14], will be discussed in Section 5.

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
Depth distribution	Nanometre films	XPS	Outer 10 nm nondestructively
		RBS, NRA	About 2 μm
		Atom Probe Tomography	up to 1 μm
		Sputter profiles using AES, XPS, SIMS	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 sections, 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 [14-16].

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 2000 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 [17-19]. 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 [20-22]. Because electrons that emerge from the material and have lost energy appear in the background region of the spectra [23], 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 [24].

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 [17, 24, 26].

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 [17, 22, 27]. 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 [17, 28] and on the web [27]. 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 [29], 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 role of XPS for these measurements was to confirm that the surface coverage did not significantly change as different cysteines were used and that they were actually attached to the surfaces of the Au nanoparticles. As a second example, a novel approach was used to create core-shell nanoparticles with apoferritin shells and $LuPO_4$ cores [30]. In this study, Lu^{+3} ions were diffused into apoferritin nanoshells and then PO_4^{3-} was added. These ions combined to form an insoluble compound in the core. TEM showed the presence of the core after the synthesis process and XPS was used to confirm the presence of Lu and PO_4. An important function of XPS in these experiments was to verify that the compounds anticipated were actually formed and remained within the nanoparticle shells.

4.2.2 Presence of contamination and coatings - Many different examples of contamination, cleaning processes, or oxidation measurements have been reported in the literature. These examples show the range of systems that can be examined. In one application, XPS and near-edge x-ray absorption fine structure (EXAFS) were used to examine the ability to remove the coating formed on Rh nanoparticles synthesized in a polyvinylpyrrolidone (PVP) containing solution [31]. The presence of a contamination layer was identified by XPS using standard analysis methods. Of equal importance, the removal of a contamination layer could be monitored [31].

Although XPS is very useful for measurement of contamination, it may not always have the spatial resolution to distinguish contamination of a substrate in the presence of a low density of particles or other objects. Because the higher spatial resolution of AES allowed surface particles to be avoided, this technique was used to monitor contamination removal and the oxidation state of a Si substrate as well as the presence of O on Pt nanoparticles [32]. Other analysis tools used in this study included AFM, scanning electron microscopy (SEM) and XPS.

4.2.3 Orientation of surface molecules - A variety of methods can be used to determine the orientation of molecules in a molecular coating on a surface including near-edge x-ray absorption fine structure (NEXAFS) [33] and optical methods such as surface-enhanced Raman spectroscopy [34]. Although XPS can be insensitive to molecular orientation in some circumstances [35], XPS can be used to determine molecular orientation for ordered molecular assemblies[36] and larger molecules with asymmetric distributions [37] of some elemental species. For ordered molecular assembles, there can be shifts in the binding energies associated with molecular orientation [36]. For the larger molecules, the primary impact is related to signal strength due to depth or layering effects as discussed above. Alessandrini et al. [37], for example, have used XPS to show differences in protein orientation on surfaces by comparing the magnitudes of N 1s photoelectron peak amplitudes. Frequently, XPS is used in combination with other methods to understand the overall composition, uniformity and molecular orientation [38]. XPS is often applied to determine molecular orientation of the relatively large molecules associated with adhesion [39]. TOF-SIMS can also be used to determine molecular ordering [40] and is sometime used in combination with XPS to identify where a molecular species is located in a film or nanoparticle [41].

4.2.4 Coating or layer thickness – There are many circumstances for which a quantitative measure of the thickness of a coating or contamination layer is useful or even essential. XPS and AES in combination with sputter depth profiles are often used to determine the thickness of coatings with thickness greater than 5 or 10 nm [42-45]. Here we focus on non-destructive methods that can be applied to films less than 10 nm thick or to coatings on particles. The relative intensities of photoelectron peaks can be used in a variety of ways to examine coating thickness for thin films and particles. XPS signal strengths have been used to quantify the thickness and layered structure of a Langmuir-Blodgett film on a glass substrate (Figure 3). This structure has been analysed by Mohai et al. [46] using XPS and a modelling program for the peak intensities called MultiQuant [47-49] to obtain information about the double-layer structure, the Pb inner layer, and the total thickness. This type of information is essential both for understanding the nature of the films as produced and for confirming the quality and reproducibility of films produced at different times or by different analysts or for determining any changes of film composition and structure with time.

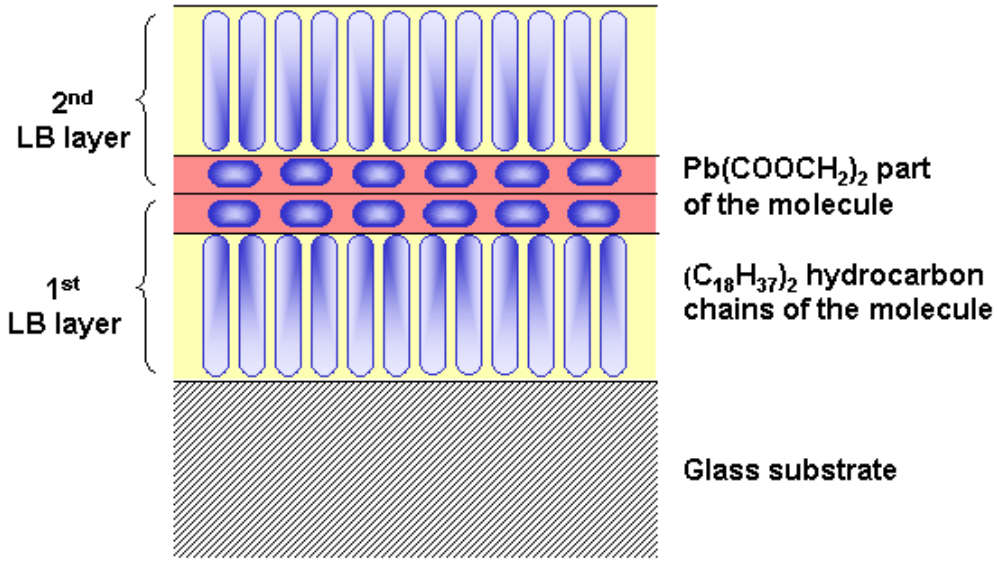


Figure 3. XPS MultiQuant was used by Mohai et al. [46] to analyse XPS data from this structure to obtain the thickness of each layer and to confirm the structure.

There has been a significant need for accurate measurements of the thickness of thin films on electronic materials, such as SiO_2 on Si. Seah and co-workers around the world have conducted an extensive set of studies on how to precisely and accurately use ratios of Si photoelectron intensities from the substrate and the oxide to determine the thickness of oxides within the thickness range of 0.3 nm to 8 nm [50-57]. They have compared XPS measurements with results of other methods and demonstrated that XPS can be highly accurate once some values of critical parameters have been determined. They have also shown that angle-resolved XPS (ARXPS) can be used to map variations in oxide thickness over a flat wafer surface [57].

When the shape of a particle is known, it is possible to obtain quantitative information on the thickness of an added coating, a contamination layer, or a particle coating using XPS [26, 58]. For the latter application, the XPS data are modelled assuming a core-shell structure for the particles. Using this method to determine the oxide-layer thickness, Yang et al. [58] were able to compare the oxidation rate for Si nanoparticles to that for silicon wafers. Figure 4 shows different changes in oxide thickness as a function of time for Si nanoparticles and for crystalline and amorphous silicon wafers.

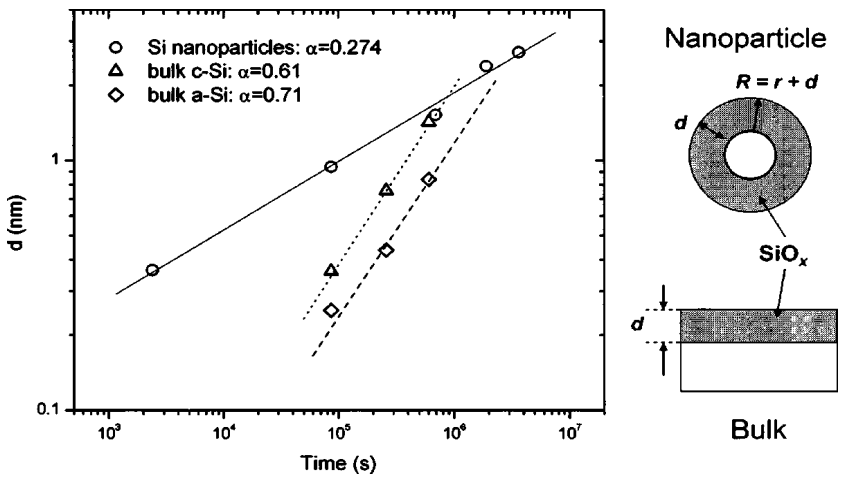


Figure 4. Comparison of changes of oxide thickness as a function of time (oxidation rates) of crystalline and amorphous silicon wafers and silicon nanoparticles using XPS measurements of peak-intensity ratios [58] to determine the oxide coating thickness. (Reprinted with permission from D.-Q. Yang, Jean-Numa Gillet, M. Meunier, and E. Sacher, *Journal of Applied Physics,* 97, 024303 (2005). Copyright 2005, American Institute of Physics.)

4.2.5 Near-surface elemental distribution – In many circumstances, elements may be enriched or depleted at the surface (e.g., of a film or nanoparticle) which may have significant impact on important chemical or physical properties. In catalysis, for example, it has been a major goal to understand the differences between bulk and surface composition and the resulting effects on surface reactions [22]. Careful consideration of signal intensity and modelling can enable a great deal of information about the distribution of a variety of elements on rather complex catalyst surface; see for example [24, 59]. Relative peak ratios can be used to determine an overall depletion or enrichment (see for example [17, 60] and references therein). Two other methods to determine relative enrichment include ARXPS [61] and the use of background signals associated with electrons that have lost kinetic energy as they leave a solid. These background or loss signals in an XPS spectrum can be used to extract information about the nature of the elemental distribution (at the nanometre scale) with depth from a surface. Although ion-sputtering depth profiles can be used to extract some of this information [44], Tougaard [23, 62] and others (as shown in Figure 5) have shown that XPS can be used to obtain quantitative information about the nanostructure of thin films from an analysis of the inelastic scattering of the emitted photoelectrons. When combined with a high-lateral-resolution methods, the Tougaard background-analysis approach can be used to obtain a three-dimensional image of the composition of the near-surface region of a complex film or material [63].

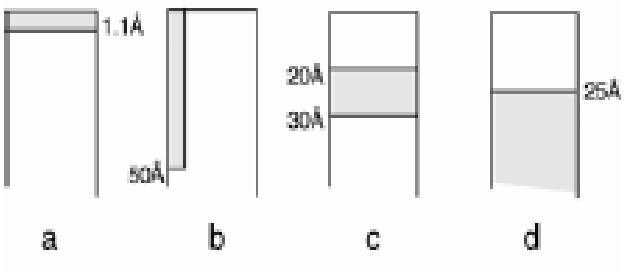


Figure 5a. These different near-surface elemental distributions of Cu in Au all produce the same Cu peak intensity.

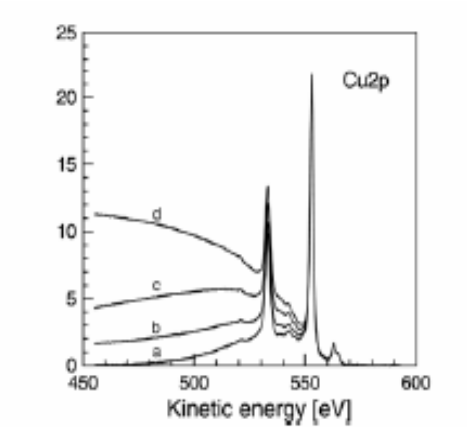


Figure 5b. Although producing the same Cu 2p photopeak intensity, the differences in background at kinetic energies below the photoelectron peak provides information on the elemental distribution with depth [23, 62].

4.2.6 Particle size - The size of nanoparticles will affect the relative strength of the signal intensities of the photoelectron peaks. This allows XPS data to be used to obtain information about particle size. For complex environments, it may be possible to obtain the size of specific nanoparticles in environments when they cannot easily be measured by other ways, including electron microscopy. As discussed in a recent review [17], a variety of approaches, initially developed for small metal-catalyst particles, have been developed to extract this information [22, 64, 65]. For example, the ratio of photoelectron intensities (from spherical particles of Cu or other metals) having different escape depths can be used to approximate the particle size [66]. Background signals can also be used to determine sizes of spherical particles on a substrate [67] with Au serving as a

specific example. In both of these approaches, it may also be useful to know particle shape which may be determined by TEM or possibly SPM.

4.2.7 Particle location, composition and shape – The lateral resolution available with the focused incident electron beam allows AES to be used to collect information about individual nanoparticles (about 30 nm or greater in size) or nanoparticle arrays. Liang et al. [68] examined the formation of Cu_2O nanodots for possible chemical or photochemical applications [69]. AES was used to examine the nature of the nanodots formed on a $SrTiO_3$ substrate after deposition using oxygen plasma-assisted molecular beam epitaxy. A secondary electron image of the nanodots and AES maps for Cu, Ti, and O are shown in Figure 6.

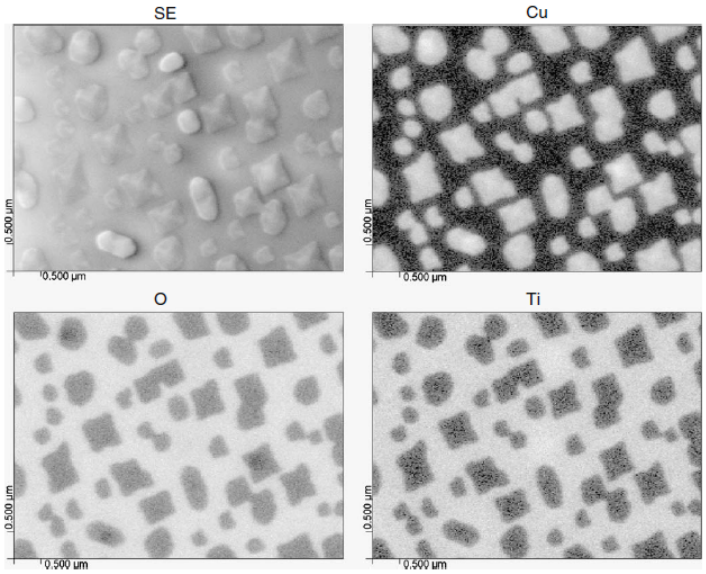


Figure 6. Secondary electron (SE) image and scanning Auger microscopy elemental maps for Cu, O, and Ti from Cu_2O nanodots grown on a $SrTiO_3$ substrate [68]. The lighter regions are enriched in the elements of interest. The Cu and Ti maps show high contrast because they are present in some areas and absent in others. The O contrast is less than in the Cu and Ti maps because O is present in both the substrate and the nanodot.

AES combined with SEM and TEM has been used to examine the location of a composite organic-inorganic nanoparticle on leukemia cells. The technique combination provided reliable high-resolution information about the nanoparticles and their binding to cell-surface antigens [70]. In this example, AES proved to be useful in spite of a coating applied to minimize charging on the biological surface. AES has also been used to measure the concentrations of Au nanoparticles grown within a polyelectrolyte matrix [71]. The need here was to identify the location and amount of gold retained on the polyelectrolyte brush surface. TEM, AFM and x-ray reflectivity measurements completed the tool set to obtain the detailed understanding of this complex nanostructured material.

4.2.8 Other properties: electronic characteristics and surface acidity - XPS or AES in combination with other methods can be used to provide information that goes beyond compositional or chemical analysis. It has been possible to use XPS signals in combination with sample substrate biasing and controlled electron flood-gun voltage to obtain electronic information from films and particles [72, 73]. By biasing a collection of nanoparticles while doing XPS, it is possible to learn aspects of the electronic properties of Au (core) silica (shell) nanoparticles. This methods works particularly well for particles embedded in a layer [73].

Determining the nature and distribution of active sites on nanostructured surfaces is an important challenge with relevance to catalysis and, possibly, particle toxicity. XPS has been used to identify and quantify the presence and distribution of Brønsted and Lewis acid sites for ZSM-5 zeolites [74]. The method involved the deconvolution of the N 1s XPS features for pyridine chemisorbed on the zeolite. Three different N states were identified and assigned to Lewis sites, weak Brønsted acid sites, and strong Brønsted acid sites. Comparison of the XPS data with IR spectroscopic data indicates that XPS could be used to both identify and quantify the nature of surface acidity.

Some additional examples of nanomaterial characterization using XPS or AES include:

Surface film or nanolayer:

- Heating-induced segregation on metal alloys [75]
- Dispersion of components in a nanocomposite film for proton-exchange membrane fuel cells [76]
- Functional group termination and the coverage of self-assembled monolayers on surfaces [77, 78]
- Properties of thin corrosion films [60]
- Stability of polymer light-emitting diodes [79]
- Thin polymer and block polymer films [80]

Nanoparticle characterization:

- Presence or removal of contamination layers [31]
- Nanoparticle size determination [66, 67]
- Electronic character of core-shell nanoparticles [73]
- Confirmation of the functionalization or measurement of the electronic structure of carbon nanotubes [81-83].

4.3 Ion-beam surface analysis methods (SIMS and LEIS)

Ion beams can be used in a variety of ways to obtain information about the nature of nanostructured materials. The most commonly used ion-beam technique is SIMS and one of the primary uses of SIMS is to extract molecular information about the functional groups and possibly molecular orientation of molecular coatings on particles surfaces.

4.3.1 SIMS and examples of SIMS applications - During SIMS measurements (Figure 1), primary ion beams of Ga^+, Ar^+, O_2^+, Cs^+, C_{60}^+, Au^+, Bi^+ or other atomic, molecular or cluster ions with energies between 3 and 20 keV are incident on the surface and the ions removed (sputtered) from the surface are detected. To extract surface molecular information, SIMS is used in a “static” mode that involves a low density and low total dose of ions such that the surface damage and alteration is minimized. Both atomic and molecular secondary ions are used to extract the surface information [84].

Like the electron spectroscopies, SIMS is also very useful for obtaining information about surface layers, functional groups added to the surface, and contamination. Two differences between the electron spectroscopies and SIMS are the high sensitivity of TOF-SIMS to many trace elements and functional groups and the changes induced to the surface due to ion sputtering. The functional-group sensitivity has been usefully applied in many ways. For example, TOF-SIMS has been used to examine peptides conjugated to gold nanoparticles as part of a protein kinase assay [85] and to examine a multilayer plasma-produced organic coating deposited on alumina nanoparticles [86]. For relatively large nanoparticles produced during welding, SIMS with sputter profiling has been used to examine the complex layers that form on the particles [47]. Unlike XPS which often infers chemistry indirectly from binding-energy shifts, SIMS has the advantage of measuring molecular fragments directly.

In addition to assisting understanding coatings or functional groups on surfaces, SIMS has proven to be equally useful for examining the basic composition of nanoparticles, both as they are being processed inside the vacuum of a SIMS system and as particles inserted for analysis. Heating a sample in a TOF-SIMS spectrometer (*in situ* thermo-TOF-SIMS) was used to examine the thermal decomposition of zinc acetate dehydrate during nanoparticle formation within a SIMS system [87]. SIMS in combination with TEM, and in-situ optical transmission spectroscopy were used to study the composition and plasmon resonance of unique ZrN nanoparticles produced by laser ablation/evaporation and adiabatic expansion from zirconium nitride powder targets [88]. TOF-SIMS has also been used to characterize the composition and oxidation state of spark-generated nanoparticles made from pairs (Ir-Ir and Ir-C) of electrodes. From detailed analysis, it was also possible to obtain information about the particle size [89]. Because many different sample and ion properties can influence the ion yields during SIMS, the technique is not inherently quantitative and quantitative measurement frequently involves reference samples of composition similar to the samples being measured.

Some additional examples of SIMS measurements on nanoparticles include

Contamination and layer structure

- Nanoparticles produced during welding - SIMS has been combined with depth profiling to examine the surface and core structure of large (300 nm) nanoparticles produced during welding [90]
- Coated nanoparticle films **–** TOF-SIMS was used to examine a thin organic coating deposited on alumina nanoparticles [86]
- Peptide –conjugated gold nanoparticles **–** SIMS was used for protein kinase assay [85]
- Urban aerosol micro- and nano-particles - Urban aerosol particles were collected in two Polish towns, Legnica and Starachowice, and characterized with mass-spectrometry methods [91]

Nanoparticle composition

- Volatile nanoparticles - TOF-SIMS and metal-assisted SIMS (Meta-SIMS) have been used to characterize the lower volatility hydrocarbons that control the formation of volatile nanoparticles during diesel engine operation [92]
- Nitride Nanoparticles – the composition of ZrN nanoparticles (5.5 to 6.5 nm) was determined using SIMS and TEM [88]
- Characterization of spark-generated **nanoparticles –** TOF-SIMS was used to characterize the composition and oxidation state of spark-generated Ir and Ir-C nanoparticles [89]*]*

Nanoparticle Formation

- Zn nanoparticles - an in situ thermo-TOF-SIMS study of thermal decomposition of zinc acetate dehydrate during nanoparticle formation [87]

4.3.2 Low energy ion scattering and applications to nanomaterials

Also known as Ion Scattering Spectrometry (ISS), LEIS is a long-established but not widely used method. However, recent developments and the availability of a fully integrated commercial instrument, have made it particularly useful because of the high sensitivity to the outermost atomic layers of a sample [12]. In LEIS, a low energy ion beam (typically an inert gas ion) is scattered mainly by atoms at the sample surface. The amount of energy lost by the ion during this scattering process is used to determine the identity of the elements present in the outermost atomic layer of the material under analysis. Only species heavier than the primary (incident) ion are detected and the mass resolution (the ability to distinguish different elements) depends on the primary ion and the mass of the species being analysed. For LEIS, low energy means ion energies less than a few thousand electron volts (which is low relative to the million electron volts typically used in Rutherford backscattering spectroscopy). The major strength of LEIS is its high surface sensitivity and specificity. This makes it a particularly useful tool for surface enrichment measurements of catalysts or a wide variety of other materials.

A particularly interesting example is the use of LEIS to examine the outer surfaces of poly(propylene imine) dendrimers. Although the different generations of dendrimer have the same overall C/N ratio, the outer C/N surface ratio changes as the dendrimers age. By combining the high surface sensitivity of LEIS with the “near” surface sensitivity of XPS, it was possible to show that dendimer aging changes primarily the outer atomic layers [93].

LEIS is another technique that does not have the resolution to examine individual particles, but can be used to measure the average size of particles and to look at changes in particle size as a function of time. It has been used, for example, to determine metal segregation and the average cluster size of $Pt/Rh/CeO_2/\gamma\text{-}Al_2O_3$

supported catalysts. The cluster size measurement was applied to atomically dispersed metals in a nanostructured catalyst and could be used to determine cluster size for particles up to 10 nm [94].

Some additional examples of LEIS measurements of nanoparticles include:

Determination of particle size

- Metal cluster size on commercial catalysts - Noble metal segregation and cluster size of Pt/Rh/CeO_2/γ-Al_2O_3 automotive three-way catalysts was studied for clusters of 10 nm and smaller [94].

Particle structure

- Internal and external structure of dendrimer box molecules – The intramolecular segregation on polymers and macromolecule dendrimers and their plasma modification were studied by LEIS and XPS [93].

4.4 Scanning probe microscopy

There are a wide variety of scanning probe microscopy (SPM) based methods of which STM and AFM are the most common examples. STM and AFM are powerful techniques that have enabled major advances in nanotechnology. This short overview cannot begin to summarize the dramatic impact they have had on advancing nanotechnology and nanoscience. The development of these “sharp” tip-based probes has made it possible for almost any laboratory around the world to examine surfaces of many types of materials with a lateral resolution approaching 1 nm for electronic properties (STM) or sample topography (AFM). AFM can provide three-dimensional imaging/visualization of nanoparticles distributed on a flat surface. SPM can provide qualitative and/or quantitative information on physical properties of nanoparticles including size, morphology, surface texture, and roughness. A variety of images can be used to extract particle-size distributions and particle volumes [95]. AFM can be conducted in vacuum, ambient conditions, liquids or other environments [96].

The application of SPM methods to nanoparticles takes many different forms [97, 98]. Many, but by no means all, applications involve examining nanoparticles on flat surfaces where many different types of information can be extracted including size and size distribution, shape (including facets), topography, and roughness. AFM has been used to examine various nanodot structures . As an example, Figure 7 shows determinations of the size and shape of Cu_2O nanostructures on a strontium titanate surface as a function of surface coverage [68]. It was possible to systematically and quantitatively determine how the shapes of these nanoparticles changed with surface coverage and growth conditions.

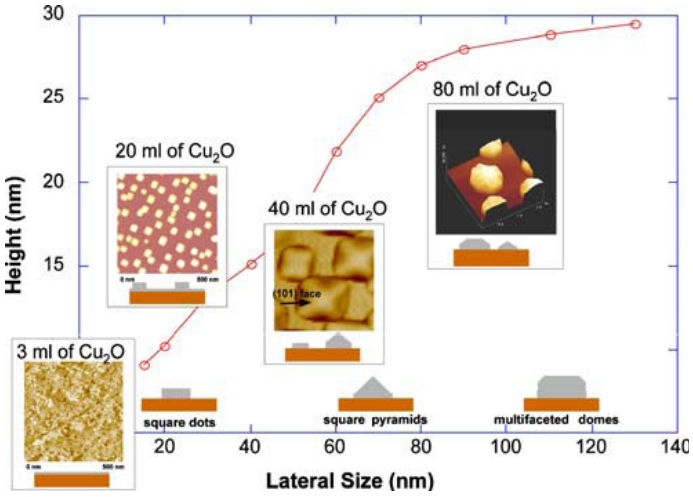


Figure 7. Plot of the lateral size and height of Cu_2O nanodots grown on $SrTiO_3$. The AFM images and schematic drawings show how the shape of the nanodots changes as an increased amount of Cu_2O is deposited on the substrate [68].

Somewhat less common applications of SPM methods have proven to have high value. Two examples are noted here. i) By attaching a nanoparticle to a scanning probe tip, it was possible to measure the interactions of individual nanoparticles with a flat surface or to other nanoparticles attached to a flat surface [99]. Such measurements provide information about reaction energies and enable these energies to be examined in different environments. ii) In some circumstances, it is useful to determine the roughness of nanoparticle surfaces; most methods for measuring surface roughness cannot be used on such samples. AFM in combination with TEM has been used to investigate the impact of synthesis processes and particle size on the surface roughness of ceria nanoparticles [100].

4.5 Surface characterization of carbon nanostructures

A wide range of tools has been applied to characterize and understand various forms of carbon nanotubes (CNTs), including single-wall carbon nanotubes (SWCNTs or SWNTs) and multi-walled CNTs (MWCNTs) as they are synthesized, functionalized and utilized in advanced materials and devices. No attempt will be made here to summarize all appropriate methods. Electron microscopy and optical methods have proven to be highly valuable [101]. However, in many circumstances surface analysis tools, also in combination with a variety of other methods, have proven to be important for collecting critical information such as surface functionalization, presence of coatings and impurities, and electronic structure [105]. Examples of such work include:

CNT and CNT-system characterization

- Plasma-enhanced CVD growth of CNTs - AES data were used to understand and optimize the growth of CNTs by PECVD [102].

Modifying CNTs – Doping, surface functionalization and charge transfer

- Diaxonium-based functionalization – XPS and GC-MS thermal analysis were used to examine the CNTs functionalized by solvent-free and aqueous-based arenediazonium. Both methods suggested that only the arcne group was retained on the CNTs [81].
- Electronic structure of Au clusters on plasma functionalized CNTs – TEM and XPS were used to study the growth of Au nanoclusters on CNTs functionalized by oxygen plasma. Core-level and valence-band measurements showed little charge transfer between the Au clusters and MWCNTs, The authors of this paper note that the uncleanliness of the surface, the presence of amorphous phases and agglomeration of as-grown CNTs appear to be constraints to CNT applications [82].
- CNT doping by encapsulation of TCNQ – Core-level and valence-band XPS in combination with near-edge X-ray absorption fine structure spectroscopy have been used to study the impact of TCNQ on the electronic structure and bonding of SWCNTs [83].
- Non-covalent sidewall functionalization of CNTs for protein immobilization - XPS and TEM provided information about the bonding of 1-pyrenebutanoic acid, succinimidyl ester to SWNTs [103].
- Nitrogen doping of CNTs – XPS was used to examine both the amount and electronic structure of nitrogen implanted into SWCNTs [104].

5 Analysis considerations, issues and challenges associated with characterization of nanostructured materials: Information for the analyst.

5.1 Introduction

Surface and interface properties play a major role in determining properties of nanostructured materials. Surface analysis provides a range of information that is more extensive than might initially be expected. The surface-analysis tools that were initially developed to obtain compositional and chemical information about thin layers or films can be extended to obtain details about the nanostructure of the films. When properly used, these techniques can provide additional information such as the presence of coatings, the coating thickness, and even electronic properties of nanoparticles. These techniques are less understood by most analysts and

thus not as frequently applied. In some cases, the methods for identifying the presence of contamination or impurities on nanoparticles do not need to be significantly different from the methods for thin-film analysis as commonly applied. Many workers, however, have shown that, with care, a great deal of additional quantitative information can be extracted from the data.

Several levels of topics need to be addressed by an analyst in characterizing nanostructured materials. These include issues of nanoparticle stability, possible impacts of the analytical probes, impacts of various types of sample handing and processing, and the effects of the environment in which the analysis is conducted. Many of the surface-analysis techniques described in this Technical Report are applied with the sample under vacuum. Since the common or "working" environment of many nanomaterials may not be a vacuum, possible impacts of removing the sample from one environment to a vacuum and the influence of the vacuum on sample properties may need to be considered. Many of these analysis issues apply to surface analysis, electron microscopy and other methods and are discussed in section 5.2. Because of the increasing awareness of the need to adequately characterize nanoparticles for environmental and health consideration and the fact that thin-layer analysis is more well established, nanoparticles are given extra attention in the following sections.

5.2 General considerations and analysis challenges

In characterizing nanoparticles or any nanostructured materials, an analyst needs to i) understand the information needed, ii) select methods that provide the required information, iii) determine how to prepare and mount the specimens to get the needed data (and avoid artefacts), and then iv) collect or assemble and analyse the data to extract the needed information. It is useful to understand the physical and chemical processes that occur during the measurements so that the data are well understood and the possible impacts of the measurements on the samples are known.

Although there are a variety of possible complications, four principles are useful in the characterization of nanoparticles:

- The more detailed information you already have about a particle (sample), the more information you can learn.

- It is important to apply multiple methods, to examine the data for consistency, and to use data from different methods to enhance the analysis (i.e., not depend on single measurements with a single method).

- Although the required data analysis may not be complex or difficult, the routine and simple data-analysis approaches commonly applied may not provide the full amount of information available.

- Although there is great value in tools with high spatial resolution, it is possible to use surface-sensitive tools (such as XPS, SIMS, and LEIS) without high resolution in all three spatial dimensions to obtain particle-size information for particle diameters less than 10 nm in circumstances when such information is not easily obtained by the high-resolution methods such as SEM, TEM or SPM.

Because nanostructured materials inherently involve samples with a high percentage of surface or interface area, the material properties are significantly impacted by the nature and properties of these interfaces in addition to any fundamental changes in material properties due to their small size. Just as many different types of information are needed about different types of nanostructured materials, there are many issues associated with the many techniques used to characterize them. Some of the topics that influence the nature and quality of the analyses of these materials (and which relate to information that can be obtained if the analysis is conducted properly) include:

• Surface layers, whether unintended contamination or deliberate additions, are often present on nanostructured materials. Coatings on nano-sized objects (for which the outer surface composition can be difficult to measure) can affect properties of the nanostructures.

• Particle shape influences surface analysis (this is readily understood for many methods and can be easily modelled).

- Nanosized objects are inherently unstable and easily change when any energy is added (e.g., due to damage or beam effects).

- Nanostructured materials vary with time and change with the environment. Such changes raise issues of sample handling and sample history.

- Nanostructured materials may adsorb solvents to a very high degree, altering properties in various ways.

- Ion beams may damage nanostructured materials at very high rates. Sputtering rates can be a factor of ten larger than for “bulk” films.

- The physical properties of nanoparticles can change with size and the environment, and some of the assumptions in the analysis (e.g., electron inelastic mean free paths) may be wrong. Samples are a polymorph of bulk materials.

- Details of the analysis environment including the presence or absence of oxygen (air or vacuum environment) and the proximity of other particles or a substrate can sometimes impact properties of nanoparticles being measured.

Scanning probe microscopies (SPM including STM and AFM) are well known to provide information from objects with nanometre dimensions. The many variants of SPM methods are very useful in characterizing nanostructures on surfaces as well as the surface topography, different types of surface domains, and even electronic and magnetic properties. Because electron beams can be highly focused, electron-beam-initiated Auger electron spectroscopy may also be readily expected to be very useful for examining particles somewhat larger than the diameter of the incident electron beam. It is considerably less apparent to many researchers that important information about nanoparticles can be extracted using XPS which generally provides information on areas larger than single nanoparticles (i.e., collections of nanoparticles). SIMS can also analyse individual particles as well as assemblies of nanoparticles over larger areas.

Challenges and approaches for using XPS to analyse nanoparticles are summarized in a web presentation prepared by D.-Q. Yang and E. Sacher at the Ecole Polytechnique of Montreal [27]. Some of the general analysis issues have been discussed in a paper by Baer et al. [3].

The following sections describe complications that can occur during surface analyses and characterizations for some samples. While it is important for analysts to be aware of the limitations of each method and of the various complications involving nanostructured samples, the surface-analytical methods can often provide unique and important information, as described in section 4.

5.3 Physical properties

Some types of analysis and characterization involve knowledge of physical parameters of the material being examined. As one example, the electron inelastic mean free path (IMFP) is important for some quantitative aspects of XPS. However, the IMFP is now determined from bulk-material properties, and may be different in samples such as a nanostructure. Several physical and chemical properties of a variety of materials change as a function of size [3] including the well-known shifts in energy levels and changes in the band-gap energy. Metal particles change their lattice parameter and sometimes their symmetry as they decrease in size. In these conditions, the particles are polymorphs of the bulk material [105] and are likely to have different physical and chemical behaviours; it is therefore reasonable that the IMFP may change. In addition, surface electronic excitations become more probable in nanostructures of decreasing size; these excitations can also modify the IMFP.

When only a single type of material is being examined as a function of size, it is often possible to measure how the properties are changing. However, if an unknown or complex material is being examined, changes in properties such as the lattice parameter or crystal symmetry could lead to confusion or to an incorrect analysis.

5.4 Particle stability and damage: influence of size, surface energy and confluence of energy scales

Some of the behaviours of nanostructured materials and related measurement issues can be understood by looking at a graph of energy versus size [3, 106]. In Figure 8, variations of thermal, chemical, mechanical, magnetic and electrostatic energies are plotted as a function of the size of an object.

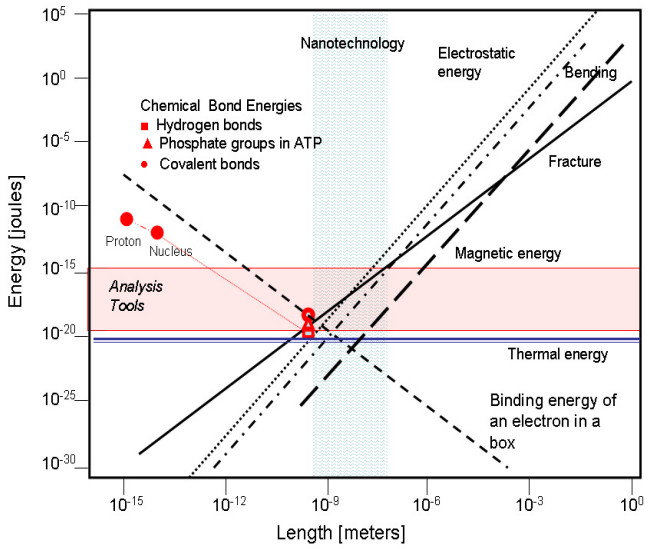


Figure 8. Variations in thermal, chemical, mechanical, magnetic and electrostatic energies as a function of the size of an object. For objects with sizes associated with nanotechnology (and many biological processes), many of these energy scales converge, thus providing increased opportunities for coupling of different excitation modes. After references [3, 106].

For objects of sizes associated with nanotechnology, many of the energy scales converge. This situation provides many opportunities for coupling of different modes of excitation. Also plotted are the energies associated with many analysis methods. These energies are equivalent to the other energies associated with the particles hinting at the significant ability of measurement probes (including x-rays, electrons and ions) to alter the properties of the object being measured. Chemical interactions with the environment or a relatively gentle heating may change the mechanical or chemical form of the object. When characterizing nanoparticles, there is a significant probability that probe effects, environmental effects, or near-neighbour effects can influence the properties of the nanosized object.

The confluence of energy scales has a significant impact on nanoparticle stability. As stated in a review article, “In the nanoworld, shape is not necessarily constant. This is because the energy of a nanoparticle shows many local-minima configurations, corresponding to different structures. A small excitation (for instance by the beam in an electron microscope) may be sufficient to induce transitions of the particle” [60]. Changes in particle shape and grain structure have been observed for metal-supported or somewhat isolated nanoparticles [107].

5.4.1 Crystal structure

In addition to particle shape and grain structure, the observed crystal structure of nanoparticles may be easily altered, even when constrained within a matrix. Among the fundamental properties of nanoparticles that change as a function of decreasing particle size are solubility, work function, and melting point. Analysis of Sn nanoparticles in a SiO_2 matrix has produced apparently conflicting results related to nanoparticle structure. A study by Zhao *et al*. [108] showed that it was possible to change the crystal structure of a nanoparticle from crystalline to amorphous and back depending on the extent of beam heating.

The lattice parameter and crystal symmetry of supported metal nanoparticles have been observed to change with particle size [109]. Because the crystal structure and lattice parameter are related to atomic binding in the particles, these changes reflect obvious changes in particle properties such as density and may relate to fundamental changes in chemical properties such as reactivity. The well-established size-induced catalytic activity of Au nanoparticles is one example of how significantly properties can alter as a function of size [110].

Specific challenges related to determining three-dimensional atomic structures of nanostructured materials have been reviewed by Billinge and Levin [13]. The physical structure of a material is a fundamental property that determines many types of material behaviour. In some cases, cleverly designed nanostructured materials involving nanoscale atomic arrangements in a background lattice or some types of nano-porous structures push or extend characterization needs beyond the ability of current tools to provide a detailed analysis. Currently there are no broadly applicable and robust methods to obtain the needed structural information for nanostructured materials. Billinge and Levin call this the *nanostructure problem* and note that "successful solutions will involve interactions among researchers from materials science, physics, chemistry, computer science and applied mathematics working within a 'complex modelling' paradigm that combines theory and experiment in a self-consistent computational framework." They also note that, similar to the experience of many researchers, no single analysis technique provides enough information to enable a unique structural determination. Although standard structural-analysis tools are important and useful for nanostructured materials, individually they are unable to provide all of the needed structural information.

5.4.2 Damage and probe effects

Although some manifestations of particle instability noted above may be reversible, (e.g., changes in particle shape or structure), sometimes clearly irreversible changes are found in the material being examined. These changes usually involve loss of information about the initial particles and, from the analysis perspective, must be considered as probe damage. Electron-beam damage to oxide shells on metallic iron nanoparticles has been observed to lead to oxidation within the vacuum of an electron microscope [111], and the structure of iron oxide nanoparticles has been shown to evolve from filled to hollow spheres due to electron-beam exposure [112]. There are probably many other types of probe damage, both reported and unreported in the literature. Table 3 gives examples of probe, environment, and proximity effects of nanostructured-material properties to show the range of phenomena possible.

In many different ways, the instability of nanostructured materials requires that new levels of caution must be applied to ensure that analysis probes (of whatever type) do not alter the characterization results and mask the information analysts are seeking to obtain.

5.4.3 Time and environment

5.4.3.1 General information

The fact that nanoparticles and other nanostructured materials often change in some way as a function of time and/or as their environments change is a direct consequence of particle stability as discussed above. However, these effects are highlighted here because of their importance to nanotechnology-related manufacturing, toxicology studies, and understanding of the potential environmental impacts of engineered nanomaterials [2]. There are two complementary aspects of this issue: i) nanoparticles made, processed and/or characterized at one time in a specific environment may not have similar characteristics or behaviours at a later time, after processing, or in a different environment (i.e., the present material may not be what was measured or determined previously); ii) Since the environment influences some fundamental behaviours of nanomaterials, properties intended or designed may differ from those expected (the redox conditions for iron oxide nanoparticles within a CNT differ from those outside a CNT).

Table 3. Examples of probe (damage), environment and proximity effects.

Probe Effects	System or material	Reference
Electron beam impact on nanoparticle shape	Au nanoparticles	[107, 113]
Electron beam melting, amorphization and crystallization of nanoparticles in a matrix	Sn nanoparticles in SiO_2	[108]
Electron-beam-induced oxidation	Fe0/FeOx core/shell nanoparticles	[111]
Ion-beam interaction and enhanced sputtering of small particles	Carbon particles	[114]
Enhanced sputtering of particles	NaCl crystals	[115]
Sputter sharpening of steep surface features	Metal pit or "anti-particle"	[116]
Probe and Environment Effects		
Solvent effects on sputtering of nanoporous materials	Nanoporous silica	[45]
Difference in the sputtering of suspended and supported carbon nanotubes	CNTs	[117]
Specimen history and coating impacts on x-ray damage	Ceria nanoparticles	[118]
Environmental Effects		
Water-driven structure changes	ZnS	[119]
Water influence on particle phase transformation	Fe_2O_3 nanoparticles	[120]
Nanotube encapsulation effect on iron oxide reduction temperature	Fe_2O_3 nanoparticles	[120]
Humidity effects on polymer nanostructures	PVB and PMMA mixtures	[121]
Surface sorbate effects on growth shape	Solution grown nanoparticles	[122]
Surface sorbate effects on particle separation	Oxide and metal nanoparticles	[123]
Environmental impact on particle chemical state	Ceria nanoparticles	[124, 125]
Thermodynamically drive adsorption and reaction	Nanocrystalline Titania	[126]
Proximity or Distance Effects		
Charge buildup or accumulation during XPS	Nanoparticles on insulating substrates and at interfaces	[127, 128]
Plasmon coupling	Au nanoparticles	[129, 130]
Coupling and engaging of quantum states	Quantum dot molecules	[131]
Impact of spacing and aggregation on magnetic properties	Iron oxide nanoparticles	[123, 132]
Interphase effects on composite properties	Nanoparticle dispersion in composites	[133]
Effect of “buffer layers” on the optical properties of silicon nanocrystal superlattices	Si rich oxide and SiO_2	[134]

5.4.3.2 Effect of environment on nanomaterial structure and properties

Some characteristics of nanoparticles are noticeably altered by changes in the environment. Although this behaviour sometimes surprises analysts and researchers, it is a direct consequence of the importance of surfaces and interfaces. From a theoretical perspective, Hill notes that "In contrast to macro-thermodynamics, the thermodynamics of a small system will usually be *different in different environments*" [135]. As the particles get smaller, the boundary (the surface or interface) is increasingly important. For example, a Langmuir adsorption model modified to include the dependence of interfacial tension (interfacial free energy) on particle size predicts an increase in the adsorption constant as the crystallite size decreases [126]. There is a growing list of experimental observations of environmentally induced changes in the physical and chemical properties of nanostructured materials systems, some of which are listed in Table 3.

Just to highlight a few examples, the structure of ZnS nanoparticles changes in wet and dry environments [119] (as illustrated in Figure 9), moisture decreases the size for which phase transitions are observed for Fe_2O_3 nanoparticles [136], humidity alters the phase structure of PVB and PMMA polymer composites [121], and small volumes in nanoporous materials absorb even volatile solvents and retain them, even in vacuum, for hours or days [45].

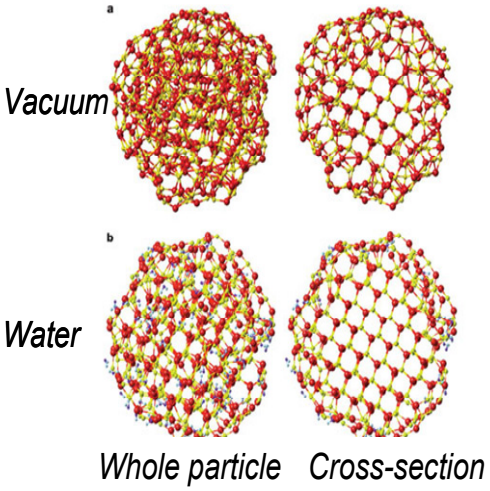


Figure 9. Model of water-driven structural transformations in nanoparticles at room temperature. In vacuum, the particle is significantly distorted relative to the bulk structure of ZnS. When water is present, the structure is similar to the expected ordered ZnS structure. From Reference [119].

These and other environmentally induced changes in nanostructured-material properties mean that there may be significant changes in the nature of nanostructured materials if they are moved into or through environments for measurement. Nanostructured materials stored in environments different from their synthesis or use may change with time. Samples synthesized and analysed in anaerobic environments may be altered if exposed to air or moist air during sample handling or mounting. Similarly, particles grown in a solution may change some properties or behaviours after drying or being placed in vacuum.

5.4.3.3 Time-dependent properties

Environmentally induced changes in nanostructured materials necessarily imply that at least some properties and behaviours will depend on time. In some cases, these materials will have a limited shelf life. Initial versions of iron metal-core oxide-shell nanoparticles produced by one vendor were initially shipped in aqueous slurry to allow for easy dispersion in solutions. However, the particles transformed from metal to oxide over time. Particles from this vendor are now routinely shipped dry or in an inert gas environment. The shelf time and the time dependence of any changes in the properties of interest as well as the lifetime of nanostructured materials can be important for both characterization and application.

The rate of material transformation upon a change in environment has not been subject to extensive study. Highly reactive materials may rapidly change upon exposure to an oxidizing environment. Such effects have been observed for reactive metal nanoparticles [16]. However, changes in the oxidation state of ceria

nanoparticles occur over periods of hours to days, depending on the synthesis solution [124]. For particles that transform rapidly upon a change in the environment, special sample transfer and storage conditions may be required. In some cases, only *in situ* measurements may provide the needed information.

5.4.3.4 Proximity effects

The properties of individual nano-sized objects can be significantly altered when they are supported on a substrate, collected into aggregates, or possibly assembled into a composite, as illustrated schematically in Figure 10. There are many different types of examples of this special environmental effect in the literature, as listed in Table 3, and many properties will be impacted by different types of nanoparticle mounting or aggregation, as suggested in Figure 10. In particular, coupling of plasmon modes in metal nanoparticles with close proximity to each other (Figure 11) provides the basis for what has been called a nanoruler [129, 130]. Particle spacing changes the electronic and magnetic properties of composites [123, 131] (Figure 12) allowing some properties of composites to be adjusted by controlling such spacing. In addition, particle-substrate interactions can lead to the build up of charge for nanoparticles supported on insulating substrates [127, 128]. Proximity effects impact the characterization of nanostructured materials by suggesting that sample mounting methods (e.g., packing particles near each other and substrate effects) can alter their behaviour and measured properties. The impacts of different analytical approaches may be indicated by the environments in which the nanosized objects may be used, collected, and characterized.

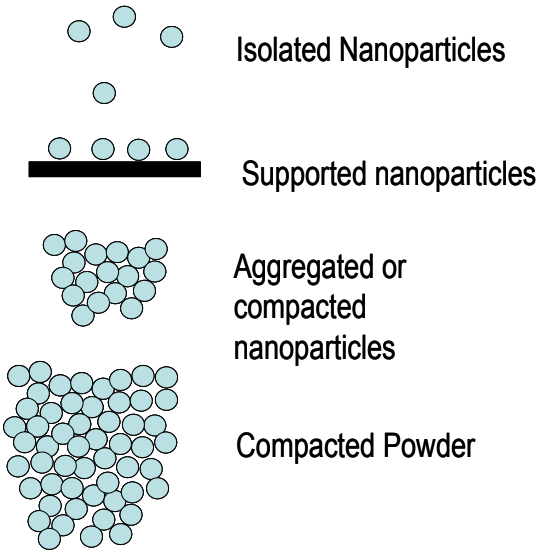


Figure 10. Illustration of different arrangements of nanoparticles that may occur depending on how the particles are collected. In some circumstances, collections of nanoparticles have properties that differ from individual particles and particle-separation distances and substrate effects can be important. (After ref [17])

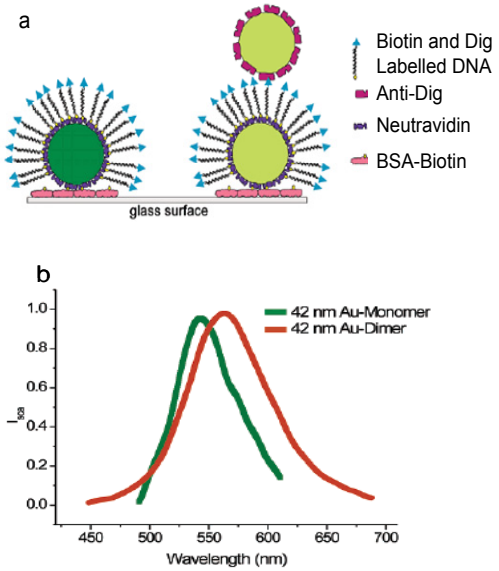


Figure 11. Plasmon coupling between Au nanoparticles is used as a molecular ruler to measure the length of a biomolecule attached to the Au-particle surface. The shift in absorption energy due to plasmon coupling for isolated and adjacent particles is determined by the particle separation. After ref [130]

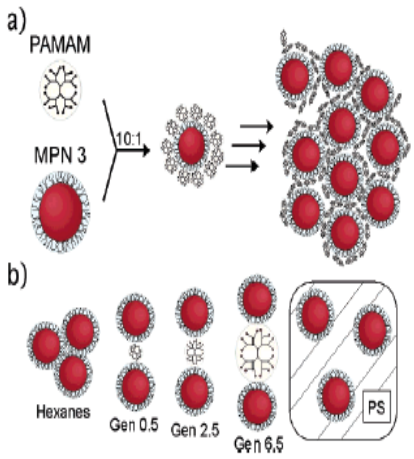


Figure 12. (a) Schematic depiction of dendrimer-mediated nanoparticle assembly. (b) Nature of dendrimer can be used to control spacing for composites. The authors used inter-particle spacing to control optical, electronic, and magnetic properties of nanoparticle composites. After ref [123]

5.5 Sample mounting and preparation considerations

The importance of contamination, impurities, and environmental effects necessarily raises issues and concerns about the handling and mounting of specimens for analysis. For nanoparticles, the issues for sample mounting are similar to those for mounting any sample for surface analysis and a number of guides have been developed [137, 138]. For the set of surface techniques discussed here, the nanoparticles being examined will normally be supported on a substrate and examined individually (e.g., by SPM and sometimes AES and SIMS) or a collection of particles will be examined. The use of vacuum-compatible tape on a substrate, solution deposition onto a substrate, or dipping a support into solution are all examples of methods used to produce nanoparticle samples for surface analysis.

Sample stability, environmental, and proximity effects discussed in section 5.4 may impact the methods and approaches required when preparing a sample for analysis. Because specific analysis needs and objectives will also play a significant role, different approaches will be required depending on the specific circumstances.

In many cases, routine sample mounting as practiced in many laboratories work very well [137]. Some of the considerations that have been shown to impact measurements in some circumstances and which may be appropriately considered are:

- Mounting of nanoparticles on insulating or metallic supports influences the information that can be extracted during XPS analysis [127, 128]
- Sample mounting density can influence the analytical method for quantification of coating for nanoparticles during XPS analysis [26]
- Understanding the character of a sample placed on a substrate can be creatively used to extract information about particle and substrate chemistry. This approach was used effectively to examine surface ligands attached to nanocrystals with TOF-SIMS [139]
- The density of nanoparticle loading on a substrate has been observed to influence the chemical information measured by XPS for ceria nanoparticles [118]
- Anaerobic handling of nanoparticle samples has preserved chemical-state information when moving from a controlled environment to an XPS instrument [14, 16]
- Different approaches for removing nanoparticles from solution for either reactivity studies or surface analysis influence the nature of the characterization results and may impact subsequent properties of the particles [140]. In some circumstances, particles need to be carefully removed from solution to stop a reaction or aging process. In other circumstances, the objective is to retain the surface chemistry.
- Biological samples often have a nanostructure. Nevertheless, a surprisingly large amount of information can be obtained from these samples with proper sample preparation and mounting methods [141]
- Examination of particles or a surface when rapidly frozen has been shown to preserve a variety of types of information about the surfaces of environmentally sensitive samples [142]

5.6 Specific considerations for analysis of nanostructured materials using XPS, AES, SIMS and SPM

5.6.1 Introduction

In addition to the general issues discussed earlier for the analysis of nanomaterials, there are specific issues that need consideration when using individual techniques.

5.6.2 Issues related to application of XPS to nanomaterials

5.6.2.1 General information

Examination of publications by year [19] show that use of XPS is increasing rapidly and that XPS is the most widely used surface chemical analysis tool around the world. Almost since the inception of XPS, the method has been applied for the analysis of nano-layers and nanoparticles. Consequently there is a great deal of experience with XPS for nanomaterial characterization, much more than for other surface chemical analysis methods with the exception of SPM. The most common application has been the characterization of complex catalyst particles which often included metal nanoparticles as the active components [22, 143, 144]. Although catalytic materials may have many of the complex structures now associated with nanostructured materials, there is now a wide variety of different types of nanostructures for which analysis is needed.

The types of information available from XPS regarding nanostructures were discussed in section 4. While most XPS analyses are conducted assuming that the sample is a uniform surface layer, the shape and structure of nanoparticles can play an important role in interpreting data from nanostructured materials [145]. Nanostructured materials do not present a uniform surface for analysis, as suggested by Figure 10. Several

analytical methods can be used to extract useful information about nanoparticles and nano-structured materials by moving beyond the uniform-layer analysis method. The appropriate approach also depends on the density and mounting of the particles.

Specific topics discussed here include: the influence of particle shape; information from a low density of particles distributed on a substrate; information from an agglomerated group of particles, and sources of binding-energy shifts.

5.6.2.2 Influence of shape

As most often applied, XPS analysis is based on the assumption that the surface is flat, smooth, and homogeneous. However, the shape of an object can play a significant role. Issues related to XPS analysis of nanoparticles and particles of different sizes have been explored by many researchers since at least the 1980s [128]. As suggested in Figure 13, a uniform coating on spherical particles on a surface would produce a different ratio of surface to substrate signals than a similar coating on a flat plate. For a particular model of a layered structure (and instrument geometry), the ratio of these signals for a flat plate, a cylinder, and a sphere are shown in Figure 14. If the whole particle is being analysed (i.e., if the particle size is smaller than the analysis area) and the particle size is larger than the electron escape depth, the ratios shown in Figure 14 are essentially independent of particle size for a wide range of sizes. However, as the particle size decreases to approximately three times the electron escape depth, this ratio begins to change (as shown in Figure 15) because some photoelectrons can travel through the whole particle. The actual ratios depend on the particular materials in the core and the shell and the photoelectron energies. Just as shape impacts XPS data, there will be shape effects, sometimes of different types, for AES and SIMS data. The routine “flat-surface” analysis approach does not always easily extend to nanoparticles.

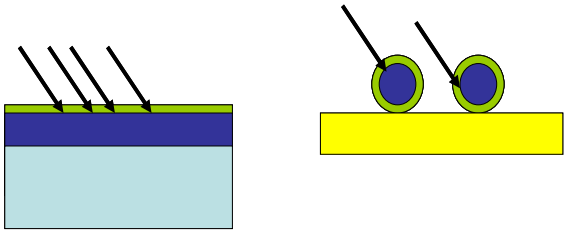


Figure 13. Schematic drawing showing a coating on a thin film and on a nanoparticle. Because of effects due to the direction of electron emission, the ratio of signals from the coating and the thin film or nanoparticle will generally differ. However it is possible to model these effects. Results of one model calculation are shown in Figure 14. (After ref [118])

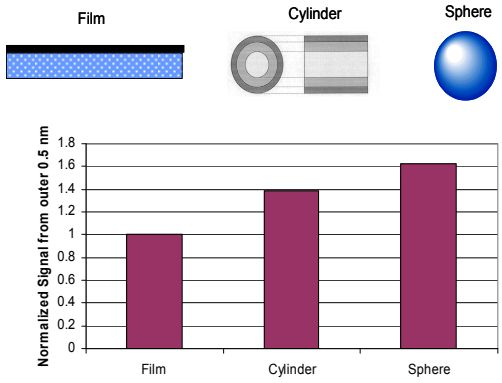


Figure 14. Diagram showing the relative intensities of surface and substrate signals for a coating on a thin film, cylindrical particle and a spherical particle. The nominal coating thickness is 0.5 nm and an IMFP of ≈1.65 nm. (After ref [17])

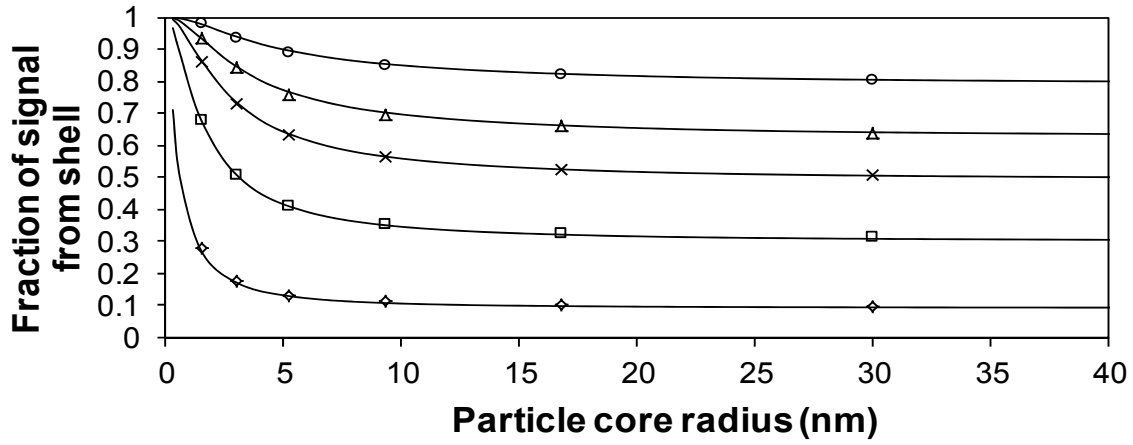


Figure 15. Fractional signals from the surface layer for nanoparticles relative to the particle core. Different curves (top to bottom) are for conditions of shell thickness = electron attenuation length = 3, 1.8, 1.2, 0.6 and 0.15 nm. Data points are from a numerical calculation and the lines from an analytical model [26]. For larger sized particles, the shape effects are relatively insensitive to the core radius. As particles get smaller and approach the electron escape depth, the relative signal from the surface layer increases.

When particle shapes are known and sometimes if the "core" compositions of nanostructures are well understood, information about shape and "bulk" composition can be combined with models of XPS structures to obtain useful information about coating thickness and possibly the structure. Such an analysis may be performed using simple signal intensities and have been used, for example, to study the oxidation of Si nanoparticles [58], as described earlier. Additional information can also be obtained by using modelling techniques such as QUASES [9,10] or SESSA [146, 147] where the background portions of photoelectron peaks comprised of electrons that have lost energy while travelling through the material can be modelled. QUASES has been used to examine the coverage of Au nanoparticles on a substrate and in special circumstances to determine particle size [67].

For nanoparticles with dimensions smaller than the electron inelastic mean free path, XPS analysis of a collection of nanoparticles might be considered or approximated as a characterization of a rough surface. The examples above demonstrated an impact of the emission angle on information about coatings and overlayers. It has been shown that the analysis of the thickness of thin overlayers on rough surfaces is roughly equivalent to collecting data at an emission angle of between 35° and 45°, sometimes called the roughness magic angle [148]. Model calculations of simple "fully three-dimensiona"l rough surfaces indicates that the thickness of an overlayer on a rough substrate can sometimes be determined reasonably well in many circumstances without taking the roughness into account in the analysis of the XPS intensities [149]. However, Olejnik and Zemek [150] showed that that this "magic angle" is not an ideal solution as it can vary with the type of surface roughness, overlayer thickness, surface contamination, an uneven overlayer thickness, and surface electronic excitations.

5.6.2.3 Low density of particles supported on a substrate

It is possible to determine the size of nanoparticles supported on a substrate by various methods. If the particles have a low density (i.e., are not overlapping), it is possible to use the peak background [67] or the ratio of two photoelectron peaks with different kinetic energies [66] from the particles to determine the particle size. An interesting feature of this approach is that the size of the particles can be determined even if they are too small to be observed by electron microscopy. With the assumption or verification that the nanoparticles are on the surface, the kinetic-energy ratio method would seem to apply to rough as well as ideally flat surfaces.

It is possible to determine the presence and even the thickness of coatings, including corrosion or oxidation layers (these are core-shell type particles) [58] using relative peak intensities. For this type of analysis, sample preparation and the nature of the substrate are of importance because particles may interact either chemically or respond physically to the substrate, and it is desirable to minimize possible overlap of peaks from particles

and the substrate. When possible, it is useful to combine knowledge about the nature of the particles and information from other techniques such as TEM to help interpret XPS data. For example, knowledge that Si will be oxidized to produce a metal-oxide shell allows a corrosion-rate calculation to be made [58]

Because a model based on the assumption of a flat surface is required to extract information from angle-resolved XPS (ARXPS), it is not possible to use angle-resolved XPS to obtain information about particle size or the size distribution [151].

5.6.2.4 Agglomerates of particles

It is not always possible to distribute particles at low density on a substrate and in some circumstances a larger number of particles is needed to obtain the desired signal strength. In a now classic study, Fulghum and Linton compared XPS analysis methods to quantitatively determine the coverage of a thin layer of particles on a substrate [152]. Although these overlayer-calculation methods are not new, they are also not widely applied as researchers ignore the possibility of obtaining useful information by this means. For nanoparticles, knowledge of coatings and/or contamination may be central to their application. For agglomerates of particles, the “roughness magic angle” approach noted earlier can be used to estimate layer coverage if the limitations of the method are considered [148, 149].

5.6.2.5 Binding-energy and peak-width changes

When performing XPS analysis of nanoparticles, it may be useful to remember that a variety of effects such as the size of particles (and interactions with the substrate) can change the binding energy and peak width of photoelectron peaks as well as change the valence-band peak shape and alter the Auger parameter [128, 145]. Not all of these effects are confined to nanoparticles as the binding energy of SiO_2 on Si varies with the film thickness due to interactions with the substrate. Therefore, not all shifts in photoelectron binding energies should be interpreted as chemical-state changes.

5.6.3 Issues related to the application of AES to nanostructured materials

Many of the considerations described for XPS apply for AES because they relate to the effects of particle size and distribution on the photoelectrons or Auger electrons detected in the experiments. However, because AES involves electron excitation, issues of scattering and transport of the primary electrons in the particle and of electrons backscattered from the substrate and then scattered or transported in the particle need to be considered [25]. Analysts often look at an SEM image and assume when collecting AES data from a feature that the detected AES signal comes only from the area irradiated by the primary-electron beam. However, when the primary beam penetrates through a nanoparticle into a substrate (or surrounding feature), Auger signals will be produced and detected from both the nanoparticle and the surrounding region [25, 153]. An ISO Technical Report is available with information on determining the analysis area in AES and XPS analyses [154] and an ISO standard gives procedures for determining the lateral resolution in such analyses [155].

5.6.4 Issues related to application of SIMS to nanoparticles

In comparison to the sputtering of flat surfaces, there are two consequences of ion impact on nanoparticles: i) enhanced sputter rates and ii) sputter-angle-induced changes in particle shapes.

SIMS measurements involve incident ions that have energies on the order of tens of keV (energies that are comparable to the cohesive energy of a nanometre-sized cluster [156]), and typical penetration lengths (for monatomic ions on flat uniform substrates) up to tens of nanometres [157, 158]. The affected area from a single collision also has a diameter on the order of one to tens of nanometres. Thus, the interaction area and energy of the primary ion is of the same order of magnitude as the size of a nanoparticle as shown in Figure 16. Simulations indicate that this situation may lead to a number of potential issues, challenges and artefacts. The primary effect that is seen through both simulation [114, 157-159] and experiment [160, 161] is that the sputter yield/rate may increase by several fold. Simulations show this effect to be due to recoil from the “back” and escape from the “sides” of the nanoparticle. It is also useful to recognize that the shape of particles will change with sputter time.

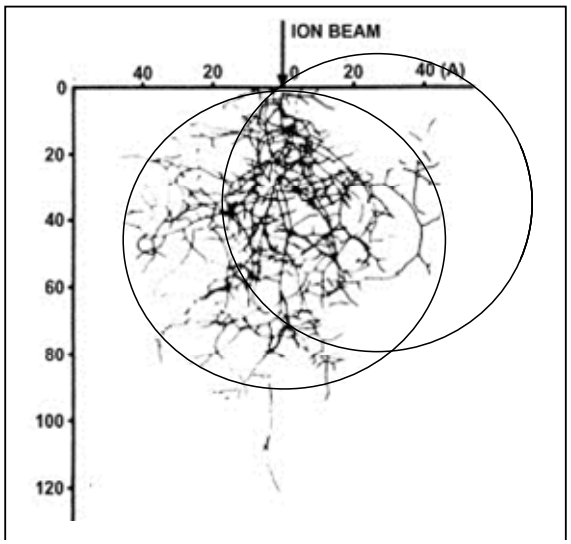
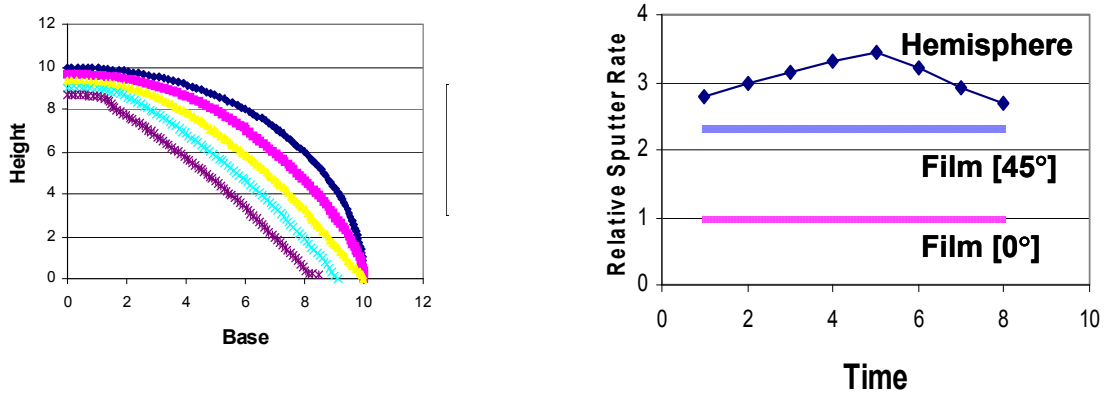


Figure 16. Monte Carlo simulations of the trajectories of ions sputtered (displaced from their initial position) by 5 keV Ar^+ striking Cu at normal incidence. The circles represent approximately 9 nm particles and show that the trajectories of many sputtered ions would intersect the surface of a nanoparticle and an enhanced sputter rate might be expected. Trajectories from Ref [158].

The enhanced sputtering of nanoparticles has a potential impact on the information that can be obtained from organic or other coatings on these particles. A static limit is identified as the ion dose below which the molecular information is typically retained and is often quoted as 10^{12}-10^{13} ions/cm^2. Because SIMS is often used to characterize functional groups associated with coatings on nanoparticle surfaces, it is desirable to stay well below the static limit and to know that this limit is significantly different for nanoparticles relative to flat surfaces. Nevertheless, data from alcohol-functionalized titanium dioxide nanoparticles covalently attached to a silicon substrate covered with native oxide and an isocyanate self-assembled monolayer suggest that the static limit for nanoparticles may not differ significantly from that of bulk materials [28].

In addition to the likely enhanced sputtering rate for nanosized objects, the significant angular dependence of ion sputtering (which is not size dependent, at least for particles > 3 times larger than the ion penetration depths) leads to highly non-uniform sputter rates for various parts of a particle. The effect of the angular dependence for sputtering of hemispheres is shown by example in Figure 17. The shape of the hemisphere changes with time and as the shape changes the overall sputter rate varies as a function of time. Note that the sputter rate for the sphere can be similar to the rate at an ion-incidence angle of 45 degrees on a flat surface, but significantly different than that observed for a normal-incidence ion. Because of the angular dependence of sputter rates, sputtering can vary as much as a factor of ten for different regions of a contoured object [116]. Such effects necessarily occur during SIMS, but would also occur if sputtering were applied during AES or XPS analysis as well.

Sample history and handling may also influence the SIMS analysis of nanostructured materials in a similar manner to that found for other surface analysis methods. One other complicating factor is that the high electric fields used in the extraction region to accelerate the secondary ions into the spectrometer may induce “field-emission” of nanoparticles.



a) b)

Figure 17. (a) Shape and (b) effective sputter rate changes during ion sputtering of a spherical particle due to typical angular variations of sputter rate. The cross section of a particle starts as a sphere and changes shape as a function of time due to the angular dependence of the sputter rate. This effect is independent of the radius of the particle with the assumption that the whole particle is being sputtered (e.g., the whole particle is within the sputter beam). Because the particle shape changes with time, the overall sputter rate also varies. Shown for comparison are the sputter rates for ions incident at different angles on a flat surface or film. (Compliments of D R Baer)

5.6.5 Issues related to the application of scanning probe methods to nanoparticles

Although a wide variety of information about nanoparticles supported by a flat substrate can be obtained using SPM methods, there are a variety of tip artefacts that can influence the accuracy of the measurements [162, 163]. Chapter 3 of Braga and Ricci is devoted to recognizing and avoiding artefacts in AFM imaging [164]. International standards committees have subcommittees working on relevant standards and guides to these effects [165, 166].

6 General characterization needs and opportunities for nanostructured materials

Some of the challenges noted in section 5 highlight important general analysis issues related to nanostructured materials. The level of detail that scientists, engineers, and manufacturers often need for physical and chemical characterization of nanostructured materials (as indicated in Tables 1 and 2) is greater than is currently feasible, particularly on a routine basis. The following list of challenges and opportunities outlines some of the important generic needs for improved characterizations of nanostructured materials:

- Because of the importance of surfaces and interfaces to the behaviours of nanostructured materials, there is a need to apply surface-analysis methods to a greater extent than is common now. The data obtained will be of increasing usefulness as more sophisticated data-analysis models are developed and applied, and particularly when results from multiple analysis methods are integrated.

- The inherently lower level of stability of many types of nanostructured materials significantly increases the attention that analysts need to pay to probe, environmental, and time effects on the materials and on the analyses of them. These issues affect procedures for sample handling, the time allowed for and nature of the analyses, and the need for comparison of results from multiple methods.

- The significant fraction of atoms or molecules associated with surfaces and interfaces increases the potential impact of surface impurities, surface segregation, or contamination on material properties.

- The environmental sensitivity of some nanostructured materials places a high value on measurements that can be made without removing the materials from the environment of interest***. In situ*** (and ***real time***) analysis methods will provide important new levels of information useful for advancing nanotechnology.

- Although there is significant need to characterize ***individual*** nanosized objects in detail, there is an equally great need to be able to characterize the critical "nano" property of a large collection of individual nanosized objects that are desired for a particular application or project of interest. For industrial applications, they may need to determine the quality of buckets or **carloads** of nanostructured materials to be used in a manufacturing process. As one specific example, consider the use of carbon nanotubes (CNTs) for which electron microscopy can be used to characterize individual or a few particles while Raman or XPS can be used to characterize defects or functionalization of a collection of particles [167, 168].

- As suggested by the *nanostructure problem* example [13] and by Grassian [5], the characterization needed for nanostructured materials often exceeds our current analytical capabilities. This situation requires new types of integration of information from more than one experimental method, the application of new and improved theoretical analyses, and the development of improved models for interpreting analytical signals from nanostructured materials.

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