Invited Paper

Surface Characterization of Nanoparticles: *critical needs and significant challenges*

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There is a growing recognition that nanoparticles and other nanostructured materials are sometimes inadequately characterized and that this may limit or even invalidate some of the conclusions regarding particle properties and behavior. A number of international organizations are working to establish the essential measurement requirements that enable adequate understanding of nanoparticle properties for both technological applications and for environmental health issues. Our research on the interaction of iron metal-core oxide-shell nanoparticles with environmental contaminants and studies of the behaviors of ceria nanoparticles, with a variety of medical, catalysis and energy applications, have highlighted a number of common nanoparticle characterization challenges that have not been fully recognized by parts of the research community. This short review outlines some of these characterization challenges based on our research observations and using other results reported in the literature. Issues highlighted include: 1) the importance of surfaces and surface characterization, 2) nanoparticles are often not created equal – subtle differences in synthesis and processing can have large impacts; 3) nanoparticles frequently change with time having lifetime implications for products and complicating understanding of health and safety impacts; 4) the high sensitivity of nanoparticles to their environment complicates characterization and applications in many ways; 5) nanoparticles are highly unstable and easily altered (damaged) during analysis.

1. Introduction – Identifying the Needs:

As pointed out by Winchester *et al*.[1] and others, the use of engineered or designed nanoparticles in consumer products is skyrocketing. Nanoparticles are routinely used in cosmetics, have great potential for medical diagnostics and treatment [2], are important components in the design of light weight strong composites, are functional components of sensors, have antimicrobial properties important to environmental safety and may be used to help remediate environmental contamination [3]. Many people see the smart application of nanotechnology as important components of clean energy production and energy storage [4]. Along with the growing actual and potential application in a variety of technologies there are concerns (both real and perceived) about environmental and health risks associated [5] with nanostructured materials because they often have properties that differ from those of bulk versions of the materials.

Along with the increased use of nanomaterials there is a growing recognition that nanoparticles and other nanostructured materials have often been inadequately characterized and that this lack of adequate characterization may limit or even invalidate some of the conclusions regarding particle properties and behavior [6-9]. Because of the identified need in technological and health and safety areas, a number of international organizations are working to establish the essential measurement requirements that enable adequate understanding of nanoparticle properties for both areas. Groups examining characterization needs for nanostructured materials include working groups of the International Bureau of Weights of Measures (BIPM), the Consultative Committee for Amount of Substance: metrology in chemistry (CCQM) [10], and the International Organization for Standards (ISO) Technical Committee (TC) 229 on Nanotechnology [11]. Specific working groups are focused on the characterization of nanoparticles for Environmental Health and

Safety (EHS) issues and for toxicology studies. Surface characterization is a subset of several analysis needs and the surface characterization needs of ISO TC 229 are being addressed in a technical report (TR14187) being prepared by the ISO TC 201 Committee on Surface Chemical Analysis. A working party on manufactured nanomaterials (WPMN) of the Organization for Economic Co-operation and Development (OECD) has established a list of physicochemical properties and material characterization needs for nanostructured materials [12].

Although there are many different information needs for nanoparticles and other nanostructured materials, there has been considerable effort to identify the most essential or required property measurements, particularly in association with toxicology studies [13], as shown in table 1. This list contains many important physical and chemical parameters relevant to characterization of engineered nanomaterials. Although size and shape are noted and important, surface properties of several types are included in the list. Because the proportion of atoms and molecules near a surface or an interface increases dramatically for nanostructured materials, it is no surprise that surface and interface properties play a significant role in determining materials behavior. The list of needed information is highly challenging in itself. However, in addition to the specific parameters, several *overarching* considerations are listed which effectively identify another set of analysis challenges that are often ignored or under appreciated. After discussing some aspects of the application of surface tools to nanoparticles, this paper highlights several topics related to these overarching considerations and how they complicate the analysis of nanoparticles and more specifically indicate both challenges and opportunities associated with surface analysis of nanoparticles.

2. Challenges

There are many different issues and challenges associated with the characterization of nanoparticle surfaces. These challenges may be grouped in different ways, some of which overlap. In the following section several specific challenges are identified and summarized. Many of these challenges have been identified in our work on iron metal-core oxide-shell nanoparticles, but have been found to apply (to differing extents) to many types of nanoparticles. These issues have been discussed in recent publications which provide more detailed information than the

Table 1 Physical and chemical properties for characterization of nanostructured materials from reference [13].

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.

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.

summaries offered here [3, 14-18]. The five specific topics discussed below identify challenges that researchers or analysts may face.

Although each topic identifies different aspects of the problem the issues are often interrelated and not independent.

1) <u>Importance of surfaces and measurement challenges</u> - Although it is widely recognized that as particle size decreases to the nanometer scale surfaces and interfaces begin to dominate and control the properties of nanostructured materials, too often efforts to characterize and understand the chemical physical nature of these surfaces and interfaces are not reported in the literature (and sometimes not measured). Grainger and Castner [6] point out that over the past 40 years surface scientists have obtained detailed knowledge about the behavior of surfaces, including the important role of deliberate and accidental surface layers. They argue that the same rigor that has been applied to surface studies is needed to understand and control the properties of nanoparticles. They called this nanosurface analysis. Such nanosurface analysis has been extensively used to characterize supported nanoparticle catalysts, but virtually unused to characterize unsupported nanoparticles in biomedical applications. Karakoti and coworkers [7] also note that the importance of nanoparticle surface chemistry, especially as applied to toxicity, has been significantly underemphasized.

An overview of the application of surface analysis methods to the characterization of nanoparticles along with their limitations and any special approaches or requirements [16] has been included as one paper in a special issue of Analytical and Bioanalytical Chemistry devoted to nanoparticle characterization. The tools discussed include electron spectroscopies (XPS and AES), incident ion methods (SIMS and LEIS) and scanning probe microscopy (STM and AFM).

The most common applications of surface methods to nanoparticle characterization appear to be associated with obtaining qualitative information about nanoparticles such as the presence of contamination, the effects of cleaning or modification processes [16, 19], to verify that the composition is that which is expected and to confirm that specific reactions have taken place [20-21]. This qualitative information is very important and provides to questions such as: "Is my sample contaminated?" Has the expected reaction occurred? Has my cleaning process been effective? Has the sample been appropriately functionalized?

In addition to answering these qualitative questions, these tools can be used to extract a good deal of additional information. Taking XPS as a specific example [15], it has been demonstrated that the nanostructure of a material influences the relative intensities of photoelectron and Auger peaks, can alter peak energies and influences the energy loss or background signals as indicated in table 2. Consequently it is possible to examine these effects to obtain information about the nanostructure of materials. Information that can be extracted includes the presence, relative surface enrichment (or depletion), oxidation state and average thickness of coatings (or shells) [22] and even the size of particles [23].

Table 2 Changes in XPS spectra due to the nanostructure of a sample [15].

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

2) <u>Nanoparticles are not created equal</u> - Small differences in similar particles may have significant impacts on particle properties. In earlier work we found that different forms of iron metal-core oxide-shell structures produce different reaction products when interacting with carbon tetrachloride (CCl_4). For some particles the breakdown of CCl_4 produces significant amount of chloroform (CCl_3H) with a reaction rate k_1 while in other cases a variety of more benign products are formed with a reaction rate k_2 [3].

$$CCl_4 \xrightarrow{k_1} CCl_3H$$

$$CCl_4 \xrightarrow{k_2} \text{Other Products}$$

In recent studies iron metal-core oxide-shell particles have been synthesized using a variation of the Schwertman and Cornell process to form ferrihydrite which was then reduced in hydrogen to produce the particles [24]. Changing the nature of the salt used in the synthesis process (sulphate, phosphate, nitrate or chloride) altered the overall reaction rate and more importantly the branching ratio ($BR = k_1/(k_1 + k_2)$) as shown in Figure 1. A BR near 1 indicates the significant production of CCl_3H while a BR near zero is producing more desirable products.

More generally, subtle differences in synthesis,

processing or storage processes can produce nanoparticles with significantly differing properties. Generic statements/conclusions about nanoparticles based on one process are not usually generic because particles produced by different processes, or with subtle differences in the "same process" are usually not equivalent. Detailed characterization may be required to know the true
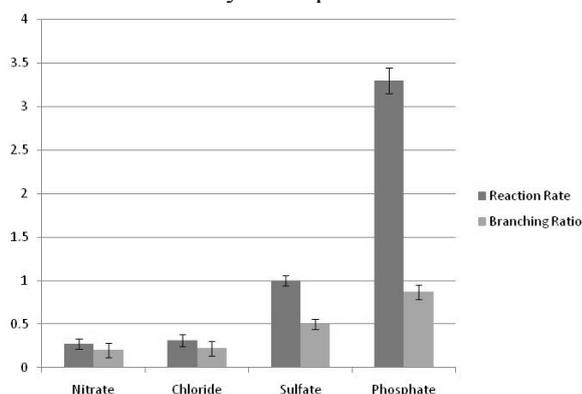
Fig. 1 The relative reaction rates [h^{-1}] and branching ratios for four different nanoparticles made by the same process (formation of ferrihydrite using an iron containing salt and reduction in hydrogen). Altering the initial salt had a significant impact of the overall reaction rate of CCl_4 with the particles in a water solution and significantly alters the branching ratio (the production of CCl_3H). Data extracted from [24].

nature of designed/engineered nanoparticles and if nanoparticles made by "identical processes" are actually equivalent. We have found that a multi-method approach is frequently needed to get a consistent accurate characterization.

3) Properties of Nanoparticles Vary with Time – For several different reasons nanoparticles are frequently not in equilibrium with their environment and properties can change as a function of time [14-16]. Time variations can occur in many ways including: particles can aggregate; particles may shrink or grow; multiphase particles may evolve as a function of time by becoming more uniform or may phase separate; particles may react with their environment to oxidize or adsorb contaminants. Consequently particle properties may have a **lifetime** and understanding the **time dependence** of the properties is important for storage/shelf life, environmental and health impacts as well as for manufacturing and product stability.

Because they are made up in part of metallic iron, it may be of little surprise that iron metal-core oxide-shell nanoparticles change both the structure of the oxide shell and the reaction properties as a function of time [18]. For these

reactive metal particles the term aging has been applied and it is important to understand the rate of aging in order to predict the lifetime and lifecycle of such particles. A different type of time dependence is demonstrated for ceria nanoparticles as shown in Figure 2. As these particles are nucleated in solution by adding peroxide to a cerium containing salt solution, they
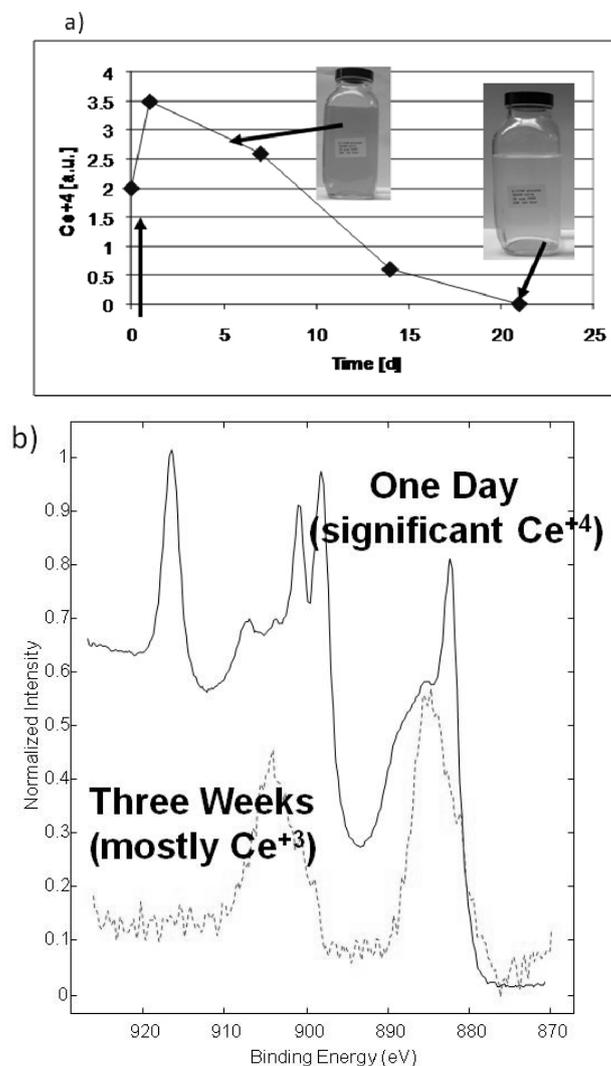
Fig. 2, a) The color of a solution containing what TEM identifies as 15-20 nm aggregates of 3-5 nm CeO_2 particles changes as Ce^{+4} converts to Ce^{+3} as a function of time as the oxidizing power of the solution decreases. b) XPS measurements of the Ce 3d photoelectron peak confirm the chemical state of the Ce as the solution color changes. The fresh solutions contain Ce^{+4} while the aged solutions are predominantly Ce^{+3}. In this case the *ex situ* XPS chemical measurements are consistent with the *in situ* optical observations – see issues in topics 4 and 5 [14].

are observed to have a yellow color indicating the presence of a significant amount of Ce^{+4} contained in the particles. As the solution ages and the oxidizing power of the solution decreases the particles convert to mostly Ce^{+3}. If peroxide is again added to the solution the particles convert

back to Ce^{+4}. Note the times associated with these changes are roughly days.

In a variety of processing, testing and storage conditions many particles will change as a function of time and understanding the rate of change is an important aspect of understanding the conditions for which particles will have the desired functionality.

4) <u>Particles respond to their environment</u> – The behaviors and properties of nanoparticles frequently change when the environment changes. Environmental effects take a number of different forms and have several different types of implications [14]. Types of environmental effects include: structure changes between vacuum and moist environment [25]; substrate or support effects [26]; changes in solution chemistry [14], and particle proximity [27] as well as more obvious effects such as corrosion or changes in surface functionality. It may be useful to indicate that the environmental dependence of nanoparticle properties is not some totally odd or unusual behavior. Hill [28] observes that the thermodynamics of nanoparticles is not the same as bulk thermodynamics, but depends on the environmental conditions. In some ways this is the same as saying that nanoparticle properties are determined by the "boundary conditions" or that "surfaces" control particle properties.

The environmental (and time dependence) behavior of many types of nanoparticles has a number of analysis and practical implications:

i) Particles can change structure and properties as the environment changes – vacuum can alter your sample.

ii) It can be important to understand the rate (time dependence) of environmentally induced changes for any particular set of particles being examined.

iii) Environmental and time effects can impact manufacturing, storage, handling and characterization. Moving from one environment to another may change particle properties. It is sometimes (or often) desirable to make measurements in working environments "*in situ*" when possible, usually in combination with *ex situ* methods. Both the XPS and TEM measurements noted in Fig. 2 require moving a sample to vacuum and the possibility of changes should be considered in the overall analysis. In this case there was a nice consistency between XPS and optical measurements. We have some indication that the TEM observations may have been impacted by sample drying.

At a 2003 National Nanotechnology Coordinating Office Interagency Research Meeting/Workshop – 'Nanotechnology and the Environment: Applications and Implications'[29], Robert Hwang, then of Brookhaven National Laboratory, observed that it was appropriate to think of nanomaterials analysis as a four-dimensional analysis rather than the more obvious two-dimensional measurement. The two expected axes or dimensions for nanostructured materials would be spatial resolution (for small objects) and energy or spectroscopy (for composition and chemical analysis). The two needed additional dimensions involved time (considering the dynamic and time variation of these materials) and environment, as discussed above. This is conceptually shown in Figure 3.
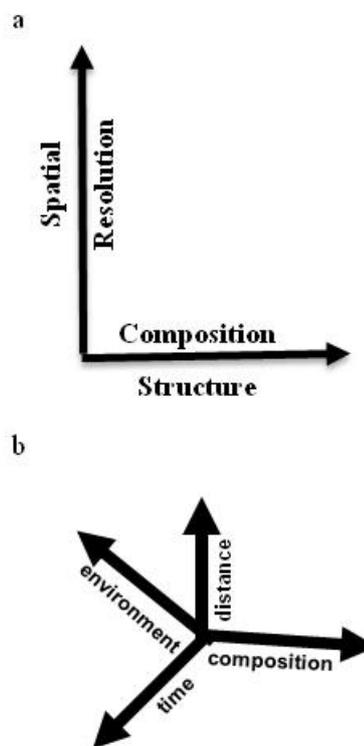
Fig. 3, a) Nanoparticles might be viewed as requiring a two dimensional characterization i) high spatial resolution (distance) and ii) composition (or structure). b) Because of the importance of environment and time, nanoparticle characterization in some circumstances may be viewed as requiring a four dimensional analysis involving i) high spatial resolution (distance), ii) composition, iii) time and iv) environment.

5) <u>Nanoparticles are often unstable and easily altered</u> – Early studies of metal nanoparticles showed that their shape and grain boundary structure can be altered during electron beam analysis [30]. The instability of nanoparticles is implied by the time and environmental variations,

but also indicates that they are highly susceptible to damage during analysis. Yacaman et al. [31] note that the energy of nanoparticles has many local minima configurations corresponding to different structures. Such shape or structural changes may have important chemical implications. In at least one catalytic reaction, catalyst shape changes appear essential for high catalytic activity [32]. Many different types of energies (fracture, bending, magnetic, thermal, bonding etc.) have been shown to have similar magnitudes for small objects [14, 33] which allow energy modes to couple. The energies associated with many types of analysis are often larger than those needed to melt or alter the shape (and possibly fracture) a particle [14].

Consequences of the unstable nature of many types of nanoparticles include:

i)   Increased probability of damage and the need to test and verify that damage is not occurring and/or to consider measurement methods that may minimize damage or damage in different way.

ii)   It is relevant to think of nanoparticles not as rigid objects but as dynamic systems.

iii)   Realize that time-dependence, environmental-dependence and damage are interrelated processes.

iv)   Recognize that processes that alter film or layers such as ion sputtering have larger effects for nanoparticles in comparison to films[16].

3. Summary and Outlook

In spite of the issues highlighted in this paper, remarkable progress had been made in synthesizing, characterizing and applying nanoparticles in many areas. These are exciting times with many opportunities related to nanostructured materials and characterization. Although real and sometimes very important challenges (analysis complications) have been identified, they do not apply equally to all materials. The importance depends on the need and the specific questions being addressed,

Many of the analysis issues discussed are not new because the catalysis community has been dealing with them for 40 years [34]. On average for fundamental research, technological applications and environmental and health questions, more and better characterization is needed (and can be done with tools we now have!). The research community is increasingly aware of what needs to be measured [9].

New tools and relevant concepts are also needed to understand the function and characteristics of nanoparticles in operating environments (*in situ*). Experimental tools/results need to be increasingly used in combination with each other but may require additional informatics approaches and linking to theory and modeling [35-36].

The intentional design of nanomaterials enhances the demands for highly accurate physical and chemical characterization (beyond that currently available) [36]. It is also important to relate these physical and chemical characterizations to measurement of the functional properties of nanoparticles to enable verification of structure-function relationships. The need for increased analysis sophistication and the application of several analysis tools stretches the capability of many researchers and research groups and highlights the importance of shared tools and expertise (such as available in instrument centers and user facilities).

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