Research Article

Characterization challenges for nanomaterials

D. R. Baer,[a]* J. E. Amonette,[b] M. H. Engelhard,[a] D. J. Gaspar,[c] A. S. Karakoti,[d] S. Kuchibhatla,[a,d] P. Nachimuthu,[a] J. T. Nurmi,[e] Y. Qiang,[f] V. Sarathy,[e] S. Seal,[d] A. Sharma,[f] P. G. Tratnyek[e] and C.-M. Wang[a]

Nanostructured materials are increasingly subject to nearly every type of chemical and physical analysis possible. Due to their small sizes, there is a significant focus on tools with high spatial resolution. It is also natural to characterize nanomaterials using tools designed to analyze surfaces, because of their high surface area. Regardless of the approach, nanostructured materials present a variety of obstacles to adequate, useful, and needed analysis. Case studies of measurements on ceria and iron metal-core/oxide-shell nanoparticles are used to introduce some of the issues that frequently need to be addressed during analysis of nanostructured materials. We use a combination of tools for routine analysis including X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and x-ray diffraction (XRD) and apply several other methods as needed to obtain essential information. The examples provide an introduction to other issues and complications associated with the analysis of nanostructured materials including particle stability, probe effects, environmental effects, specimen handling, surface coating, contamination, and time. Copyright © 2008 John Wiley & Sons, Ltd.

Introduction

Significant advances in current technologies (mostly as important but evolutionary improvements) and the potential for more revolutionary impacts in areas such as clean energy production, electronics, medicine, and environment (sometimes as a basis for radically new technologies or approaches to manufacturing) have fueled major research and development efforts in nanotechnology around the world. This immense amount of research necessarily involves applications of many types of characterization of manufactured and natural nanostructured objects. Environmentally related research on properties of nanostructured materials in our laboratories and the research of users at the Environmental Molecular Sciences Laboratory (EMSL), U.S. Department of Energy (DOE) User Facility have demonstrated that frequently, there are surprising challenges and complications associated with the characterization of many types of nanostructured materials. Although many of these challenges and complications are well documented in the literature, they appear in unexpected ways in new research or new materials and therefore, frequently surprise many researchers. In this article, we summarize some of the effects observed in our work and others reported in literature.

Challenges and frequently unmet analysis needs associated with the characterization of nanostructured materials have been highlighted in recent review papers and in the technical press. A March 2006 article in Small Times Magazine described a workshop designed to identify roadblocks to nanobiotech commercialization[1] and noted the opinion of several experts that many of the important physical characteristics needed to understand the physical and chemical properties of nanoparticles are unreported in research reports and apparently often unmeasured, especially in areas related to assessing 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. In a review article on nanoparticle synthesis, Finke notes that '*Many researchers continue to work with compositionally poorly characterized nanoclusters made by unbalanced reactions leading to nanoclusters of unknown composition.*'[2]

Two Case Studies

Some of the issues related to characterization challenges can be introduced by examining two specific materials that present different analysis challenges: (i) the effect of the local environment on the chemical state of ceria nanoparticles and (ii) the time dependence of the properties of iron metal-core/oxide-shell nanoparticles in solution.

*   Correspondence to: D. R. Baer, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Box 999 MS K8-87, Richland WA, 99352, USA. E-mail: don.baer@pnl.gov

a   Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland WA, USA

b   Fundamental and Computational Science Directorate, Pacific Northwest National Laboratory, USA

c   Energy and Environment Directorate, Pacific Northwest National Laboratory, USA

d   Advanced Materials Processing and Analysis Center, Mechanical Materials Aerospace Eng, Nanoscience and Technology Center, University of Central Florida, Orlando Florida, USA

e   Department of Environmental and Biomolecular Systems, Oregon Health and Sciences University, Beaverton Oregon, USA

f   Physics Department, University of Idaho, Moscow, Idaho, USA

Environmental impacts on ceria nanoparticle chemistry

Because of the potential impacts of nanostructured ceria materials (including their possible importance for fuel cells[3] as catalysis supports,[4] as corrosion inhibitors,[5] and as antioxidant biomaterial[6]), they have been examined by a variety of researchers. Much of this research involves ceria nanoparticles and it is important to understand the effect of size, environment, and time on their properties. While many reports discuss the size, structure, and morphology dependent properties[7–10] of this functional oxide, less attention is given to the influence of local chemistry and time. Researchers have often used the optical absorption properties to interpret the band gap of ceria nanoparticles and have calculated the particle size from these data with the help of effective mass approximation theory. However, results from different groups, using a variety of synthesis processes, determine highly variable band gap energy shifts (or no shifts), some of which are attributed to quantum confinement.[11–13] Although it is recognized that several competing factors may impact the measurements[11] including variations in the amount of Ce^{+3} contained in the particles,[13] there is a general lack of consistency with the effective mass approximation and some authors[13] expressed the hope that detailed theoretical analysis would be useful to resolve the issues.

In one part of our research, we have observed the ability of the local chemical environment to drive chemical changes in ceria particles.[14] These observations and the related UV-Visible transmission spectra suggest that some behavior interpreted in literature as quantum confinement might also result from oxidation state changes in ceria nanoparticles, switching between Ce^{+3} and Ce^{+4}. Nanoparticles have been synthesized in different ways and are often studied after different amounts of processing; they may have been precipitated, cleaned, dried, coated with a surfactant, and re-suspended in various solvents before they are characterized. Our experience suggests that particle processing can lead to chemical modification of ceria nanoparticles and hence, the resulting properties. The possibility of such an effect has not usually been clearly accounted for in reported results. To understand these possible effects, we have examined ceria nanoparticles under as-synthesized conditions (*in situ*) in various environments,[14,15] and correlated these with *ex situ* measurements.

Ceria nanoparticles were synthesized in de-ionized (DI) water (18.2 MΩ), without any additives or surfactant micelles. A Ce(III) precursor nitrate solution was oxidized with stoichiometric quantities of H_2O_2. The oxide nanoparticles were found to nucleate immediately following oxidizer addition.[15] UV-visible transmission spectra at this time, collected from a slightly yellow-colored suspension, showed a combination of Ce^{+3} and Ce^{+4} characters, although predominately Ce^{+3}. After 1 day, the suspension turned a strong orange–yellow color, consistent with a predominant Ce^{+4} oxidation state of the nanoparticles (Fig. 1). When the suspension was aged for more than 2–3 weeks, it turned colorless with no visible precipitation. UV-visible transmission data for this aged solution indicated that the oxidation state was predominantly Ce^{+3}. Transmission electron microscope (TEM) images of the particles indicated that they were comprised of 20–100 nm aggregates made up of about 3 nm grains. Because the particles appeared to be identical for all solution conditions, within a couple of hours after nucleation the color changes and UV-visible results were not due to changes in particle size. Ceria nanoparticles synthesized in glucose, dextran, and poly (ethylene glycol) have also been examined, and demonstrate similar behaviors, but over different times.[14,15]
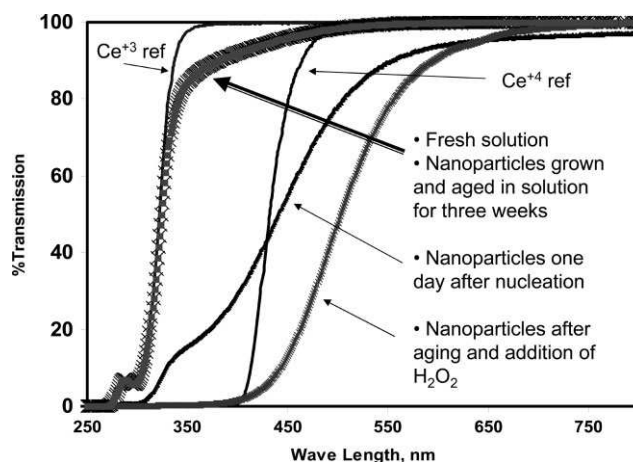

Figure 1. UV-visible transmission through solutions containing Ce salts and Ce-oxide nanoparticles. The particles were nucleated by adding H_2O_2 to a $Ce(NO_3)_3$ 6 H_2O solution. Immediately after adding the peroxide, the solution differed slightly from the $Ce(NO_3)_3$ 6 H_2O Ce^{+3} reference. Nanoparticles were immediately nucleated and after 1 day, they had significant Ce^{+4} characteristics. After three weeks in solution, they had primarily Ce^{+3} characteristics. When an oxidizing agent (H_2O_2) was added, the chemical state of the particles returned to Ce^{+4} over a period of hours. TEM data indicates that the base particle size does not change significantly after a few hours of nucleation.[15]

In separate studies, we have oxidized the precursor using bases such as ammonium hydroxide. While the nanoparticles synthesized using H_2O_2 showed the oxidation state switching, the particles prepared using a base did not show noticeable signs of color change indicative of any changes in the oxidation state for approximately 2 months. This implies that the nanoparticles of ceria are stable as Ce^{+4} as long as they are in an oxidizing environment. This tendency has been confirmed by the re-appearance of Ce^{+4} in the 3-week aged water-based ceria suspensions, described above (Fig. 1), with the addition of H_2O_2. The real-time *in situ* UV-visible transmission results were totally consistent with the XPS measurements made after removing particles from solution (Fig. 2). While the oxidation switching phenomena was found to occur irrespective of the solvent, in acidic conditions (pH 2–4), the relative amount of Ce^{+4} was found to vary with each additive.

These observations, based around very simple *in situ* optical measurements, demonstrate the influence of particle environments on nanoparticle chemistry. The time and local environment-dependent chemistry eventually controls the UV-absorption capability and other properties of ceria nanoparticles. A clear understanding of the possible interaction between the ceria nanoparticles and the solvents in which they are suspended will be important in effectively utilizing their properties. The interpretation of the optical absorption (or other characterization) data without accounting for the actual chemical changes might mask some important features of the nanomaterials. This study highlights the dynamic nature of nanoparticles, including the effect of the particle environment, and suggests that environmentally induced changes of particle chemistry could complicate analysis of the UV-visible transmission data. The combined use of several methods was required to get needed information along with application of an *in situ* method to allow for time-dependent measurements in the environment of interest.
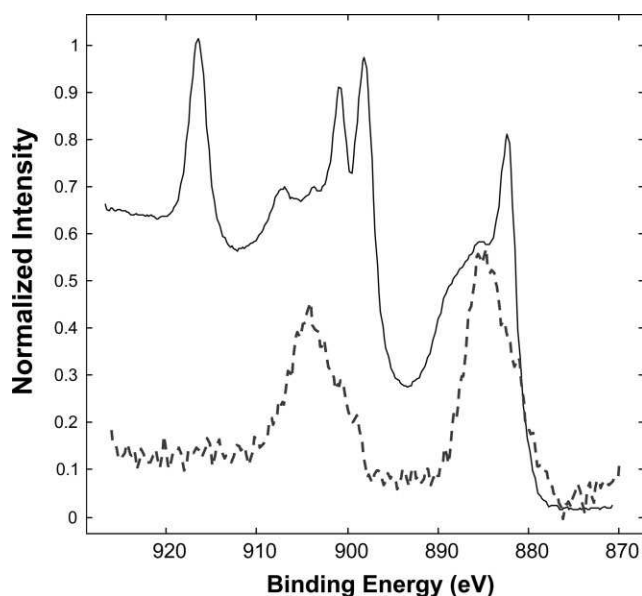
Figure 2. XPS spectra of the Ce 3d photoelectron peaks from a solution aged 1 day (solid curve) and a solution aged several weeks (dashed curve). The spectrum from particles after 1 day shows significant Ce^{+4} character of the Ceria particles (for more details on features of the Ce 3d peak structure, see Henderson *et al*.[16]), consistent with the optical transmission data. After significant aging, a predominantly Ce^{+3} character appears in the XPS spectrum of the particles, also consistent with the optical data.

Time-dependent properties of Fe nanoparticles

Iron metal-core/oxide-shell nanoparticles,[17–19] are currently the subject of significant research because of their possible roles in environmental remediation, medical diagnosis and treatment, and for use in magnetic storage media. In earlier work[17] we reported that the XPS spectra of iron nanoparticles removed from storage or synthesis solution and introduced into the spectrometer without air exposure have a significant metallic signal, while air exposure of 1 min (or less) can significantly decrease or remove the metallic character as seen in the 2p region of the iron photoelectron spectra. In contrast, iron core/shell particles reported in work by Kuhn *et al*.[20] were stable with time and environmental exposure. A time dependence of the properties of nanoparticles may limit the areas of their possible application. At the very least, the impact of particle size, particle environment, and the role of the particle synthesis process on any time-dependent behavior need to be understood and possibly controlled.

We have been studying reactive properties of iron core/shell nanoparticles for reduction of chlorinated hydrocarbons that can contaminate ground water. Our specific work has involved study of the reactivity of iron core/shell nanoparticles with CCl_4 in water. During this process, the metallic core of the particles becomes oxidized and the contaminant reduced. Earlier work demonstrated that the reaction pathways for the breakdown of CCl_4 were altered by the nature of the nanoparticles being tested.[17] Because the properties of the oxide shell may have a significant influence on both the reaction rate and pathway, we are particularly interested in understanding how the oxide shells change with time and in comparing the rates of corrosion of different types and sizes of nanoparticles. Determining oxidation and corrosion rates for nanoparticles is somewhat more complex than determining corrosion rates for larger flat samples.[21] Here we compare the oxidation rates of two differently sized nanoparticles,

prepared by two different processes, in DI water. Reactivity studies conducted on these particles show significantly different reaction rates. The corrosion studies were undertaken to help understand the reactivity differences.

One type of nanosized iron metal-core/oxide-shell nanoparticle (Fe^{H2}) was obtained from Toda America, Inc. (Schaumberg, IL) This material was produced by reduction of goethite and hematite particles with H_2 at high temperatures (200–600 °C) and stored as a dry powder under anaerobic conditions. TEM images of the initial starting material (e.g. Figure 3(a)) show the material to be made up of somewhat irregularly shaped metal particles of 40–100 nm in size. The center of the particles was, as expected, metallic Fe which was coated with a crystalline oxide shell roughly 2–3-nm thick. Analysis of the line-widths in the XRD pattern using the Scherrer equation indicated metallic Fe with an ∼40–50-nm crystallite size and oxide (magnetite or maghemite) with a crystallite size of ∼3 nm. Thus the XRD and TEM pictures of the Fe^{H2} particles are quite consistent. These particles are made by a commercial vendor and have been found to be highly reactive to CCl_4.[17]

The second type of particle was produced by a sputter-gas-aggregation process in vacuum Fe^{SP}.[18,22] The TEM images indicate that these are core/shell particles made up of ∼10–14 nm particles with ∼2–3-nm thick oxide shells. The XRD data (line width and ratio of metal to oxide) are also quite consistent with the TEM data. A typical TEM image from this type of particle is shown in Fig. 3(b). These small particles were collected on a silicon wafer. Tests of the reactivity of these particles indicate very little overall reactivity with CCl_4 in marked contrast to Fe^{H2}. One hypothesis for the difference is that the somewhat purer, smaller Fe^{SP} particles have a more protective oxide shell and thus may have an overall slower corrosion rate and breakdown of the initial oxide shell.

Nanoparticles of both types (Fe^{H2} and Fe^{SP}) were exposed to DI water. After exposure for the specified time, the samples were removed from solution and dried by rinsing with a solvent. These samples were then examined by XRD to determine the relative amounts of metallic iron and magnetite. Because of limited sample material, the film of Fe^{SP} particles was exposed to solution several times to produce the aggregate exposure. Although not reported here, selected samples were also analyzed by TEM and XPS.

The TEM examination of a particle of Fe^{H2} after exposure to water for 24 h is shown in Fig. 3(c). After 24 h, the oxide was no longer a simple, coherent apparently dense shell. It appears to have thickened and is more porous and less ordered. The mole fraction of Fe observed by XRD in the form of oxide is plotted as a function of solution exposure time in Fig. 4. Note that the initial fraction of Fe as oxide is consistent with the expected core-shell structure having metal cores coated with approximately 3-nm oxide shells. Also shown are curves modeling the corrosion of the nanoparticles, with the assumption that the particles are round and that all of the oxidized metallic iron is converted to (observable) oxide. The model assumes a constant corrosion rate and considers that the Fe^{H2} particles were initially approximately 80 nm in diameter (74-nm core with a 3-nm coating) and the Fe^{SP} particles were 11 nm in diameter (5-nm core with a 3-nm shell). As can be observed from the plot, the corrosion rates determined differ by a factor of 3 and 4 between more rapidly oxidizing Fe^{H2} and slower reacting Fe^{SP}.

Because we needed to handle the Fe^{H2} particles slightly differently than the film of Fe^{SP} particles, we consider this data to be preliminary in nature. Nevertheless, the slower oxidation rate for the Fe^{SP} particles is consistent with the independently observed low reactivity of these particles with CCl_4 in solution. Obtaining
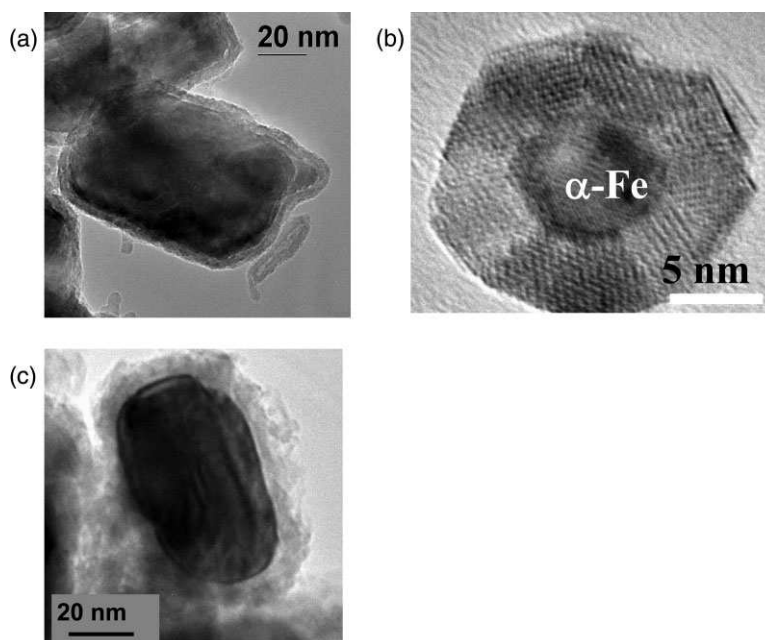
Figure 3. (a) TEM image of an initial Fe^{H2} nano ~40 × 80 nm^2 particle showing a compact oxide shell and metal core; (b) TEM image of an initial Fe^{SP} nano ~13-nm diameter particle showing a compact oxide shell and metal core; (c) TEM image of Fe^{H2} nanoparticle exposed to DI water for 24 h showing a less ordered and expanded oxide shell.

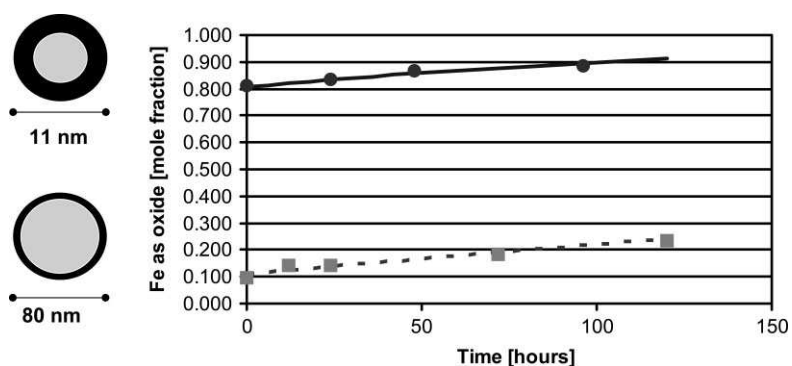**Figure 4.** The mole fraction of oxidized iron in collections of Fe^{SP} (●) and Fe^{H2} (■) nanoparticles initially and as a function of time exposed to DI water. The oxide to metal ratio was determined from XRD data using Jade v. 7.5 (Materials Data, Inc., Livermore, CA). The lines are from a model of corrosion of nanoparticles with the sizes schematically shown in the figure. The model assumes a constant corrosion rate (nm/h) and that all of the oxidized metal converts to oxide that can be observed by XRD. The corrosion rates in the model were adjusted to get a reasonable fit to the data. The inferred oxidation rate for the Fe^{H2} particles (dashed line) is ~0.02 nm/h and that of the Fe^{SP} particles (solid line) is ~0.006 nm/h.

an approximate corrosion rate for the differently sized particles required linking a model that included particle size and shell thickness to experimental data. The consistency between the XRD and TEM data regarding the amount of oxide and size of the metal cores helped determine a self-consistent understanding of the initial particle structures. Several sets of XPS data were also consistent with a core-shell structure, since most of the signal was for oxidized Fe with a small Fe^0 signal to support the thin shell picture.

This example indicates the importance of linking experiment and models to understand the behavior of nanostructured materials along with the frequent necessity of integrating several types of information from different techniques to obtain a self-consistent picture of the materials. The example again demonstrates that nanostructured material may change with time and those changes can vary depending on the material and the environment. Unlike the ceria nanoparticles, the changes observed for these core-shell particles are not readily reversible. With the

increasing use of different forms of nanostructured materials, understanding their fate and function as a function of time in different environments may be very important. In recent work on Fe^{H2} particles, we have examined the time dependence of the reaction rate, the branching ratio, and hydrogen evolution, as well as the XRD and TEM data noted here.[23]

Generic characterization issues and challenges

The above case studies indicate some of the potential impacts of the environment and time on the properties of nanostructured materials. We, and many others, have observed a variety of other that may complicate analysis of nanostructured materials. These include environmental interactions, interactions of the materials with the experimental probes used to make the measurements, and the manner by which the materials are processed and mounted for analysis.

These more general issues and challenges associated with the analysis of nanoparticles are explored in the following sections as three inter-related topics:

1. What makes it nano? Why do we care that it is nanosized?
2. Stability: probe damage and environmental effects
3. Proximity effects – impacts of separation, aggregation, and supports

What makes it nano?

The sizes for which particle or material properties change depend upon the material and the property of interest. An example set of materials along with the sizes at which some important properties undergo changes is shown in Fig. 5. Without describing each effect in detail, it is apparent that some properties of metal particles change for sizes below ~5 nm, while a variety of oxide properties change at sizes of tens of nanometers. There are many reports of the synthesis of nanostructured materials in literature that provide no information about the properties or range of properties that are impacted by the size. As noted earlier,[1] size often matters, but information about how size is important is often missing and, as suggested by the study of ceria nanoparticles, can be difficult to accurately determine. Although there can be many different reasons for changes in particle behavior, three different cases are noted here: (i) impact of size when material properties remain constant (classical behavior); (ii) changes in behavior when material properties are essentially unchanged, but some characteristic length is approximately equal to particle size (quantum confinement); and (iii) fundamentally new material properties because of the small object size.

Classically some particle properties are expected to vary with decreasing particle size because of the impacts of surface energy.

One example of this behavior is the solubility of quartz crystals which increases as particle size decreases following the modified Kelvin equation.[32] In a second example, the phase stability of titania nanoparticles in solution is dominated by the surface energy.[33] This type of behavior does not depend on any change in the fundamental properties of the material as size decreases, but results from the change in surface area to volume ratio. This classical effect is due to the increasing importance of surface energy as particle size decreases. Deviations from these classical properties can provide the basis for truly revolutionary material behaviors.

To understand the importance of the impact of the behaviors of nanostructured materials, it is necessary both to understand the impacts of size from a classical view and to determine if additional effects are present. This type of consideration is nicely demonstrated in the work of Campbell *et al.*[25] examining the surface energies of Pb nanoparticles. Using calorimetric measurements, they showed that the energy dependence of supported Pb particles varies much more quickly than predicted by the Gibbs-Thompson equation.

The energy levels of quantum dots are the most common examples of a particle property change due to a characteristic length, in this case, the electron wave length is approximately equal to the particle size.[34,35] Another critical length effect is the increased sputter rates for particles when the projected range of the impact ion is roughly equal to the particle size.[36] Both the changes in energy states due to quantum confinement and the size variation in sputter rate occur when the particle size is approximately comparable to some relevant length (electron wavelength or ion projected range) and the effects vary monotonically with particle size.

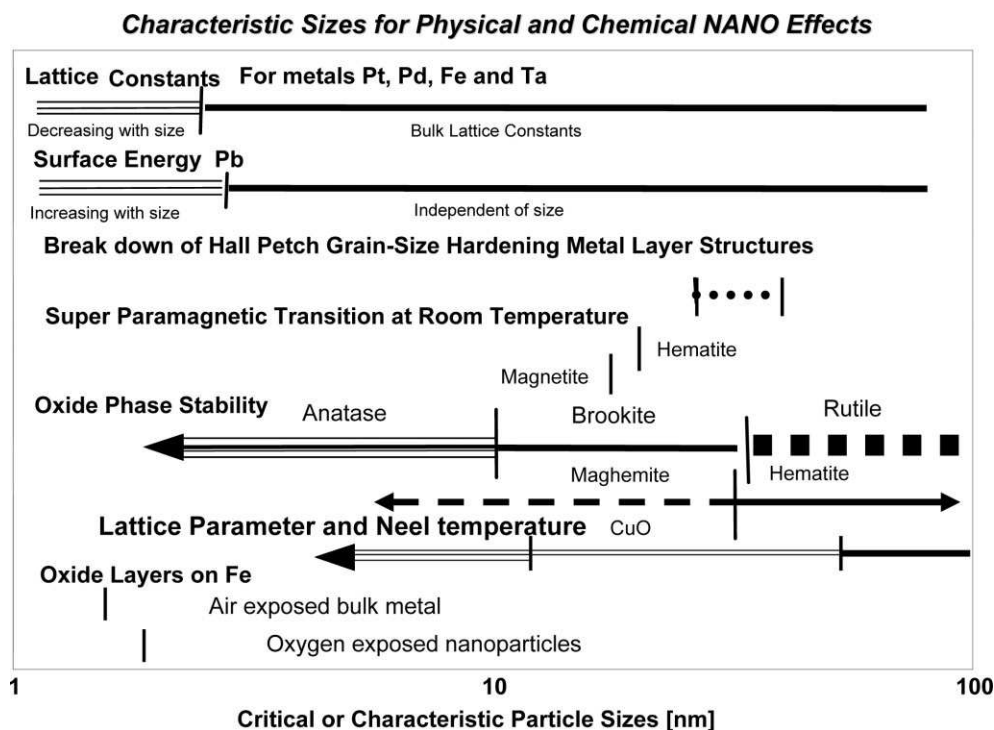Many researchers consider true nanoscience phenomena to be observed when fundamentally new types of properties are

Figure 5. Diagram showing characteristic sizes for which some physical, chemical, or other properties of objects are altered. The sizes for which properties are altered depend upon the material and the specific property. This information was extracted from many sources including lattice constants,[24] surface energy,[25] Hall-Petch breakdown,[26] superparametric temperatures,[27] hematite-maghemite phase transition,[28] TiO₂ phases,[29] CuO,[30] and oxide film thickness on Fe.[31]

present that are not simply scalable with particle size such as those observed for catalytically active Au nanoclusters.[37] In the 1983 Faraday Lecture entitled 'The Molecular Theory of Small Systems' Rowlinson[38] noted that in some circumstances for small systems, some of the thermodynamic functions of importance such as pressure and energy density are not uniquely defined and that when an object size is less than the correlation length, statistics and thermodynamics lose their meaning. Objects in this size range are of great interest and potential importance. However, they are likely to be more difficult to describe and more difficult to create, store, characterize, and to control.

The usefulness of papers reporting on the synthesis and characterization of nanomaterials will be increased to the extent that researchers can identify and report the nature of the material properties that are influenced or controlled by the nanosized features of the materials. Especially, as nanomaterials are transferred from research to technological application, it is essential to understand and be able to measure and report the characteristics of the material that lead to desired or useful properties.

Stability: probe damage and environmental effects

As shown by both the ceria and iron nanoparticle examples, it can be important to recognize that many nanosized objects are not unique stable entities. The existence of stable or meta-stable states with similar energies[39] and the fundamental characteristics of the thermodynamics of small objects implies that nanosized objects can be very easily altered. When considering the nature of the thermodynamics of nanosized systems, Hill observed that the thermodynamics of a small system will usually be different in different environments.[40]

Some of the unexpected stability and environmentally sensitive behaviors of nanostructured materials at times are enabled by the approximately equivalent magnitudes of several types of energy. In a review article on the biological frontiers of physics, Phillips and Quake[41] present a graph that nicely shows that values of several types of energy converge as the sizes of objects approach those we associate with nanotechnology. An altered version of their graph is presented in Fig. 6. Using specific examples (e.g. the electrostatic energy of a spherical shell, the fracture and bending for a rod with a 20/1 length ratio), they show that the magnitudes of thermal, chemical, mechanical, and electrostatic energies are very similar for nanosized objects. We have added energies associated with several types of analysis methods and the magnetocrystalline energy of particles.[42] Phillips and Quake describe the impact of the size and energy plot for biological processes thus: '*As the characteristic size approaches that of biological macromolecules, all energy scales converge. This convergence is an opportunity for complex physical phenomena and processes that are utilized by life.*' This same size range is characteristic of nanostructured materials and the convergence of the energy scales enables energy of one type to be converted to energy of other types using chemical, physical, or biological processes. We generally expect, for example, that adding a small amount of energy to a material will cause an insignificant rise in the temperature. However, for nanoparticles and some nanostructured materials small amounts of energy may readily change their shape or structure. Many analysis techniques involve a significantly larger energy than those associated with nanoparticles, and they may have significant impact on what is measured.

The experimental implications of these effects take many forms some of which are highlighted below. An important message is that in several circumstances the shape and other properties
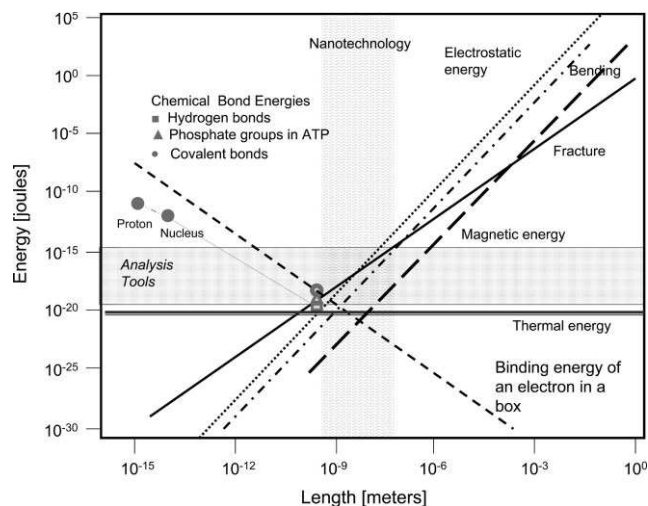

Figure 6. Variations in thermal, chemical, mechanical, magnetic, and electrostatic energies as a function of the size of an object. For objects of the sizes associated with nanotechnology (and many biological macromolecules), many of these energy scales converge providing increased opportunities for coupling of different types of excitation modes. This figure was developed from a figure of Phillips and Quake.[41] Items added to the original figure include the magnetocrystalline energy[42] based on a K value of 1000 J/m^2 and energies associated with experimental probes $\sim$5–10 000 eV.

of nanoparticles must be considered to be dynamic rather than static. In some cases the dynamic behavior may be an essential useful character of the nanostructured material. For example, dynamic shape changes appear to be necessary for catalysts used in growing carbon nanotubes to function.[43]

Probe effects

Probe and environmental effects raise important challenges to analysis or characterization of nanostructured materials. A few examples are listed in the first section of Table 1. The use of an electron beam has been observed to influence the shape and structure of isolated metal nanoparticles,[39,44] to melt or induce recrystallization of Sn particles in silica,[45] and to damage the protective oxide on Fe^0/FeO_x core/shell nanoparticles enabling oxidation in the vacuum within a TEM.[46] In some circumstances electron beam-induced modification of nano-objects may be used to tailor the structure of the objects in a controllable way. This has been demonstrated in the Fe-oxide nanoparticle system.[47]

The impact of ions on nanostructured objects will be influenced by object size,[36] shape (due to angle of impact effects),[48,49] as well as other physical characteristic effects such as how the objects are supported[51] or if they are porous.[50] The two latter characteristics may lead to environmental effects as objects suspended in space respond differently to an ion beam than when they are supported on a substrate, and a porous structure may adsorb and retain ambient gases or solvents for considerable time in vacuum.

Probe effects on nanostructured materials are not limited to those that might be expected due to electron or ion irradiation. Although x-ray damage during analysis is well known, it is less common than ion or electron beam damage and often not carefully considered.[66,67] We have observed changes in the ratio of Ce^{+3} to Ce^{+4} as a function of x-ray exposure for ceria nanoparticles removed from solution and deposited on a Si substrate for analysis.[52] We found it disturbing that the fraction of Ce^{+3} relative

Table 1. Examples of probe, environment, and proximity effects

Probe effects	System or material	Reference
Electron beam impact on nanoparticle shape	Au nanoparticles	[39,44]
Electron beam melting, amorphizing, and crystallization of nanoparticles in a matrix	Sn nanoparticles in SiO_2	[45]
Electron beam-induced oxidation	Fe^0/FeO_x core/shell nanoparticles	[46]
Ion beam interaction and enhanced sputtering of small particles	Carbon particles	[36]
Enhanced sputtering of particles	NaCl crystals	[48]
Sputter sharpening of steep surface features	Metal pit or 'antiparticle'	[49]
Probe and environment		
Solvent effects on sputtering of nanoporous materials	Nanoporous silica	[50]
Difference in the sputtering of suspended and supported carbon nanotubes	Carbon nanotubes (CNTs)	[51]
Specimen history and coating impacts on x-ray damage	Ceria nanoparticles	[52]
Environmental effects		
Water driven structure changes	ZnS	[53]
Water influence on particle phase transformation	Fe_2O_3 nanoparticles	[28]
Nanotube encapsulation impact on iron oxide reduction temperature	Fe_2O_3 nanoparticles	[54]
Humidity effects on polymer nanostructures	Poly (vinyl butyral) (PVB) and poly (methylmethacrylate) (PMMA) mixtures	[55]
Surface sorbate effects on growth shape	Solution grown nanoparticles	[56]
Surface sorbate effects on particle separation	Oxide and metal nanoparticles	[57]
Environmental impact on particle chemical state	Ceria nanoparticles	[14,15]
Proximity or distance effects		
Charge buildup or accumulation during XPS	Nanoparticles on insulating substrates and at interfaces	[58,59]
Plasmon coupling – basis of a nanoruler	Au nanoparticles	[60,61]
Coupling and engaging of quantum states	Quantum dot molecules	[62]
Impact of spacing and aggregation on magnetic properties	Iron oxide nanoparticles	[57,63]
Interphase effects on composite properties	Nanoparticle dispersion in composites	[64]
Effect of 'buffer layers' on the optical properties of silicon nanocrystal superlattices	Si-rich oxide and SiO_2	[65]

to Ce^{+4} measured by XPS in a collection of 3-nm nanoparticles increased during x-ray exposure. The 3-nm particles, which showed an *increase* in the relative amount of Ce^{+3}, had been grown in a solution containing toluene.[52] In contrast, for a similar sample preparation and XPS analysis of ceria nanoparticles approximately 10 nm in size, produced in a solution containing no added organic solvent (only water), the amount of Ce^{+3} *decreased* with time during x-ray exposure. We attribute these differences to the nature of the surface coatings (particle environment) on the two types of particles. In one case, the coating is organic and upon irradiation, the particles are further reduced. In the second case where the surface coating is water or OH^- species, the particles are oxidized upon irradiation. Regardless of the detailed mechanism, there were x-ray damage effects during analysis of both types of particles and the synthesis history and local chemical environment of the particles altered the effect of the probe.

Environmental effects

The initial examples and theoretical considerations have already introduced the potential importance of the environment on

properties of nanoparticles, examples of which are also listed in Table 1. For nanostructured materials with highly reactive components, the high surface and interface areas of nanostructured materials should lead to a high expectation of environmentally induced changes. High reactivity is an important issue for analysis of some materials regardless of the unit or particle size, but such effects may be enhanced for nanosized objects of materials that are usually less reactive. In some other circumstances, environmental effects may lead to unexpected nanomaterial properties. In addition to changing the reduction conditions for iron oxide,[54] environmental effects include the impact of water on the atomic structure of ZnS nanoparticles[53] and phase transitions for hematite nanoparticles,[28] the influence of humidity on polymer nanocomposite structure,[55] as well as the effects of surface adsorbates on particle shape[56] and separation.[57]

In summary, it is important for researchers to recognize the potential influence of analysis probes and particle environments on the characterization of nanostructured materials. Although such concerns apply to other materials, they apply especially to nanostructured materials. At a 2003 National Nanotechnology Coordinating Office Interagency Research Meet-

ing/Workshop – 'Nanotechnology and the Environment: Applications and Implications', Robert Hwang observed that it was appropriate to think of nanomaterials analysis as a four-dimensional analysis rather than the obvious two-dimensional. 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.

Proximity effects – impacts of separation, aggregation, and support

Although the properties of individual nanoparticles are easy to model, in many cases, analysis of particles and other nanostructured objects involve some type of 'support' or collection of material. In effect, the environment of individual nano-objects may include the presence of a support substrate, a matrix, or other nearby nano-objects. In some cases, the properties of the overall 'system' being analyzed may be significantly influenced by the separation distances (proximity) involved. This might be considered as a generalization of the environmental effect.

Examples of a few proximity effects are also listed in Table 1. The impact of final state or initial state charging is well known for the analysis of isolated clusters in vacuum. Wertheim and Dicenzo[58] examined both the signal strength and changes in photoelectron binding energies for supported nanoparticles and pointed out the importance of charge accumulation during XPS of isolated nanoparticles supported on insulating substrates. In this case, the nature of the substrate will impact the XPS binding energy measurements on the nanoparticles. In a more recent work, Suzer's group has looked at interface charging in different types of systems involving nanoparticles.[59] More generally, as nanoparticles become closer together, their magnetic, electronic, and optical properties may be altered. The coupling of quantum states of small particles as they approach each other is the subject of fundamental study.[62] When Au nanoparticles are near each other in solution, an extended plasmon band can be observed that does not appear for isolated nanoparticles.[60] Proximity-induced plasmon coupling provides the basis for a nanoruler.[61,68]

Magnetic coupling between nanoparticles may seem less of a surprise than electronic coupling. Rotello's group has systematically used molecular spacing units to control nanoparticle separation in films made up of nanoparticles.[69] Included in their studies is the impact of spacing of iron oxide nanoparticles on the blocking temperature.[57] A number of interesting issues related to nanoparticle synthesis and characterization were noted in the work by Schwartz *et al.*[63] They found that the location of Co in doped ZnO nanoparticles influenced the UV-Vis absorption spectra and that surface Co on nanoparticles influenced the results differently than the Co within the nanoparticles. For their work, they used a chemical treatment to remove the surface Co. They also observed that particle aggregation in solution (due to aging) totally altered the magnetic behavior. When particles were allowed to aggregate, ferromagnetism was observed, while for disperse nanoparticles only the properties of isolated paramagnetic dopants were observed.

Nanocomposites of various types are being assembled to generate new materials with novel or advanced properties. The distribution of nanoparticles (as well as their size) can significantly alter the mechanical and electronic properties of polymer composites because of the impact of the interphase

region around the nanoparticles.[64] The 'buffer' layers surrounding Si nanoparticles play a significant role for the optical properties of a silicon nanocrystal superlattice.[65]

The important impact of proximity effects in analysis of nanostructured materials is that packaging, processing, handling, and mounting of these materials for analysis can alter the results of the measurements.

Conclusions and Opinions

Research involving nanostructured materials is increasingly important around the world for a wide variety of technologies. The expanded need for information, analysis, and characterization of these materials presents a wide variety of challenges introduced by the fundamental natures of nanostructured materials, some of which appear not to be fully recognized by parts of the research community.

Particularly important are considerations associated with particle stability, probe-induced alternations, the impact of sample history and previous processing, and the frequent time-dependent properties of these materials. Environmental and time-dependent behaviors effectively increase the need for application of real-time and *in situ* analysis methods in addition to careful application of *ex situ* methods.

Although advanced analysis methods and visualization tools have enabled many aspects of nanoscience and nanotechnology, there are fundamental issues and significant development needed to enable the collection of adequate information about the many types of nanostructured materials, either those already created or simply imagined by researchers around the world. Specific issues related to determining three-dimensional atomic structures of nanostructured materials were recently reviewed by Billinge and Levin.[70] Cleverly designed nanostructured materials involving nanoscale atomic arrangements in a background lattice or some types of nanoporous structures push or extend needs beyond the ability of current tools to provide detailed analysis. Currently, there are no broadly applicable and robust methods to obtain the needed structural information for nanostructured materials. Billinge and Levin[70] 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 modeling" paradigm that combines theory and experiment in a self-consistent computational framework.' This model equally applies to analysis needs related to local chemical properties and other likely areas.

Careful analysis of nanostructured materials generally requires application of several complementary analysis methods. In many cases, the most useful information requires expert application of the methods. Often, imaging methods such as electron or scanning probe microscopy must be coupled with surface chemical analysis (e.g. XPS or other) or bulk analysis (e.g. XRD) to obtain both representative and interpretable results. The combination of the need to apply several analysis methods and the need for expert application stretches the ability and expertise of individuals and groups and should encourage collaboration and/or interaction with expert staff at user and other facilities.

In many circumstances, not enough attention is being paid to the characterization and impact of surface layers, coatings, and contamination on the properties of nanostructured materials.

Acknowledgements

References

[1] Candace S. *Small Times Magazine*. March 17, 2006.
[2] Finke RG (ed.). *Synthesis, Characterization and Applications*. Marcel Dekker: New York, 2002.
[3] Zhu B, Yang XT, Xu J, Zhu ZG, Ji SJ, Sun MT, Sun JC. *J. Power Sources* 2003; **118**: 47.
[4] Kawi S, Tang YP, Hidajat K, Yu LE. *J. Metastable Nanocryst. Mater.* 2005; **23**: 95.
[5] Patil S, Kuiry SC, Seal S, Vanfleet R. *J. Nanopart. Res.* 2002; **4**: 433.
[6] Das M, Patil S, Bhargava N, Kang JF, Riedel LM, Seal S, Hickman JJ. *Biomaterials* 2007; **28**: 1918.
[7] Deshpande S, Patil S, Kuchibhatla S, Seal S. *Appl. Phys. Lett.* 2005; **87**: 133113.
[8] Mai HX, Sun LD, Zhang YW, Si R, Feng W, Zhang HP, Liu HC, Yan CH. *J. Phys. Chem. B* 2005; **109**: 24380.
[9] Feng Z, Siu-Wai C, Jonathan ES, Ebru A, Qiang J, Richard DR, Irving PH. *Appl. Phys. Lett.* 2002; **80**: 127.
[10] Feng XD, Sayle DC, Wang ZL, Paras MS, Santora B, Sutorik AC, Sayle TXT, Yang Y, Ding Y, Wang XD, Her YS. *Science* 2006; **312**: 1504.
[11] Zhang YW, Si R, Liao CS, Yan CH. *J. Phys. Chem. B* 2003; **107**: 10159.
[12] Masui T, Fujiwara K, Machida Ki, Adachi Gy, Sakata T, Mori H. *Chem. Mater.* 1997; **9**: 2197.
[13] Hernandez-Alonso MD, Hungria AB, Martinez-Arias A, Coronado JM, Conesa JC, Soria J, Fernandez-Garcia M. *Phys. Chem. Chem. Phys.* 2004; **6**: 3524.
[14] Karakoti AS, Kuchibhatla S, Babu KS, Seal S. *J. Phys. Chem. C* 2007; **111**: 17232 – 17240.
[15] Kuchibhatla S, Karakoti AS, Seal S. *Nanotechnology* 2007; **18**.
[16] Henderson MA, Perkins CL, Engelhard MH, Thevuthasan S, Peden CHF. *Surf. Sci.* 2003; **526**: 1.
[17] Nurmi JT, Tratnyek PG, Sarathy V, Baer DR, Amonette JE, Pecher K, Wang CM, Linehan JC, Matson DW, Penn RL, Driessen MD. *Environ. Sci. Technol.* 2005; **39**: 1221.
[18] Qiang Y, Antony J, Sharma A, Nutting J, Sikes D, Meyer D. *J. Nanopart. Res.* 2006; **8**: 489.
[19] Zhang XX, Wen GH, Huang SM, Dai LM, Gao RP, Wang ZL. *J. Magn. Magn. Mater.* 2001; **231**: L9.
[20] Kuhn LT, Bojesen A, Timmermann L, Nielsen MM, Morup S. *J. Phys.: Condens. Matter* 2002; **14**: 13551.
[21] Yang DQ, Gillet JN, Meunier M, Sacher E. *J. Appl. Phys.* 2005; **97**: 024303. DOI:10.1063/1.1835566 .
[22] Baer DR, Tratnyek PG, Qiang Y, Amonette JE, Linehan JC, Sarathy V, Nurmi JT, Wang CM, Antony J. In *Environmental Applications of Nanomaterials: Synthesis, Sorbents and Sensors*, Fryxell G, Cao G (eds). Imperial College Press: London, 2006.
[23] Sarathy V, Tratnyek PG, Nurmi JT, Baer DR, Amonette JE, Wang C-M, Chun NC, Penn RL, Lai G, Reardon EJ. *J. Phys. Chem. C* 2008; (in press), DOI: 10.1021/jp0777418.
[24] Nepijko SA, Klimenkov M, Adelt M, Kuhlenbeck H, Schlogl R, Freund HJ. *Langmuir* 1999; **15**: 5309.
[25] Campbell CT, Parker SC, Starr DE. *Science* 2002; **298**: 811.
[26] Hoagland RG, Kurtz RJ, Henager CH. *Scripta Mater.* 2004; **50**: 775.
[27] Krishnan KM, Pakhomov AB, Bao Y, Blomqvist P, Chun Y, Gonzales M, Griffin K, Ji X, Roberts BK. *J. Mater. Sci.* 2006; **41**: 793.
[28] Chernyshova IV, Hochella MF, Madden AS. *Phys. Chem. Chem. Phys.* 2007; **9**: 1736.
[29] Ranade MR, Navrotsky A, Zhang HZ, Banfield JF, Elder SH, Zaban A, Borse PH, Kulkarni SK, Doran GS, Whitfield HJ. *Proc. Natl. Acad. Sci. U.S.A.* 2002; **99**: 6476.
[30] Punnoose A, Magnone H, Seehra MS, Bonevich J. *Phys. Rev. B* 2001; **64**: 174420.
[31] Antony J, Qiang Y, Baer DR, Wang CM. *J. Nanosci. Nanotechnol.* 2006; **6**: 568.
[32] Hochella MF. *Earth Planet. Sci. Lett.* 2002; **203**: 593.
[33] Finnegan M, Zhang H. *J. Phys. Chem. C* 2007; **111**: 1962.
[34] Reed MA. *Sci. Am.* 1993; **268**: 118.
[35] Reed MA, Randall JN, Aggarwal RJ, Matyi RJ, Moore TM, Wetsel AE. *Phys. Rev. Lett.* 1988; **60**: 535.
[36] Jurac S, Johnson RE, Donn B. *Astrophys. J.* 1998; **503**: 247.
[37] Hakkinen H, Yoon B, Landman U, Li X, Zhai HJ, Wang LS. *J. Phys. Chem. A* 2003; **107**: 6168.
[38] Rowlinson JS. *Chem. Soc. Rev.* 1983; **12**: 251.
[39] Yacaman MJ, Ascencio JA, Liu HB, Gardea-Torresdey J. *Journal of Vacuum Science and Technology* 2001; **19**: 1091.
[40] Hill TL. *Nano Lett.* 2001; **1**: 111.
[41] Phillips R, Quake SR. *Phys. Today* 2006; **59**: 38.
[42] Bao YP, Beerman M, Krishnan KM. *J. Magn. Magn. Mater.* 2003; **266**: L245.
[43] Ajayan PM. *Nature* 2004; **427**: 402.
[44] Smith DJ, Petfordlong AK, Wallenberg LR, Bovin JO. *Science* 1986; **233**: 872.
[45] Zhao JP, Chen ZY, Cai XJ, Rabalais JW. *J. Vac. Sci. Technol., B* 2006; **24**: 1104.
[46] Wang CM, Baer DR, Amonette JE, Engelhard ME, Antony JJ, Qiang Y. *Ultramicroscopy* 2007; **108**: 43.
[47] Latham AH, Wilson MJ, Schiffer P, Williams ME. *J. Am. Chem. Soc.* 2006; **128**: 12632.
[48] Gaspar DJ, Laskin A, Wang W, Hunt SW, Finlayson-Pitts BJ. *Appl. Surf. Sci.* 2004; **231 – 232**: 520.
[49] Chen HH, Urquidez OA, Ichim S, Rodriguez LH, Brenner MP, Aziz MJ. *Science* 2005; **310**: 294.
[50] Gaspar DJ, Engelhard MH, Henry MC, Baer DR. *Surf. Interface Anal.* 2005; **37**: 417.
[51] Jung YJ, Homma Y, Vajtai R, Kobayashi Y, Ogino T, Ajayan PM. *Nano Lett.* 2004; **4**: 1109.
[52] Baer DR, Engelhard MH, Gaspar DJ, Matson DW, Pecher K, Williams JR, Wang CM. *J. Surf. Anal.* 2005; **12**: 101.
[53] Zhang HZ, Gilbert B, Huang F, Banfield JF. *Nature* 2003; **424**: 1025.
[54] Chen W, Pan XL, Willinger MG, Su DS, Bao XH. *J. Am. Chem. Soc.* 2006; **128**: 3136.
[55] Gliemann H, Almeida AT, Petri DFS, Schimmel T. *Surf. Interface Anal.* 2007; **39**: 1.
[56] Scher EC, Manna L, Alivisatos AP. *Philos. Trans. R. Soc. Lond. A* 2003; **361**: 241.
[57] Frankamp BL, Boal AK, Tuominen MT, Rotello VM. *J. Am. Chem. Soc.* 2005; **127**: 9731.
[58] Wertheim GK, Dicenzo SB. *Phys. Rev. B* 1988; **37**: 844.
[59] Dane A, Demirok UK, Aydinli A, Suzer S. *J. Phys. Chem. B* 2006; **110**: 1137.
[60] Norman TJ, Grant CD, Magana D, Zhang JZ, Liu J, Cao DL, Bridges F, Van Buuren A. *J. Phys. Chem. B* 2002; **106**: 7005.
[61] Reinhard BM, Siu M, Agarwal H, Alivisatos AP, Liphardt J. *Nano Lett.* 2005; **5**: 2246.
[62] Bayer M, Hawrylak P, Hinzer K, Fafard S, Korkusinski M, Wasilewski ZR, Stern O, Forchel A. *Science* 2001; **291**: 451.
[63] Schwartz DA, Norberg NS, Nguyen QP, Parker JM, Gamelin DR. *J. Am. Chem. Soc.* 2003; **125**: 13205.
[64] Liu H, Brison LC. *J. Appl. Mech.* 2006; **73**: 758.
[65] Glover M, Meldrum A. *Opt. Mater.* 2005; **27**: 977.
[66] Baer DR, Engelhard MH, Lea AS. *Surf. Sci. Spectra* 2003; **10**: 45.
[67] Baer DR, Gaspar DJ, Engelhard MH, Lea AS. *Beam Effects During AES and XPS Analysis*. IM Publications and Surface Spectra: Chichester, 2003.
[68] Liu GL, Yin YD, Kunchakarra S, Mukherjee B, Gerion D, Jett SD, Bear DG, Gray JW, Alivisatos AP, Lee LP, Chen FQF. *Nat. Nanotechnol.* 2006; **1**: 47.
[69] Verma A, Srivastava S, Rotello VM. *Chem. Mater.* 2005; **17**: 6317.
[70] Billinge SJL, Levin I. *Science* 2007; **316**: 561.