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COMMERCIALLY MANUFACTURED ENGINEERED NANOMATERIALS FOR ENVIRONMENTAL AND HEALTH STUDIES: IMPORTANT INSIGHTS PROVIDED BY INDEPENDENT CHARACTERIZATION

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Abstract—Environmental and health studies on nanomaterials are appearing in the literature at a rapid pace. These studies will address important issues related to the environmental health and safety (EHS) of nanomaterials. As noted in many recent workshop and agency reports, studies devoted toward the environmental fate and transport, nanomaterial–biological interactions, toxicity, and overall risk assessment of nanomaterials should have nanomaterial characterization as a central component of the study design. This aspect of the study design is necessary so that risks associated with nanomaterials can be fully understood and related to specific material properties. For studies that use commercially manufactured nanomaterials, the company often provides characterization data (e.g., chemical composition, phase, and size) of the purchased materials. One question is, how good are these data? Another is, what methods of analysis are used to characterize the properties of commercial nanomaterials? In the present study, some examples are presented that show marked differences between independent characterization of commercially manufactured nanomaterials and that provided by the company. Furthermore, information provided by the manufacturer may be incomplete and nonrepresentative of the entire sample and, in some cases, the information can, in fact, be wrong. Thus, the current study demonstrates an important need for independent characterization data in EHS studies of purchased materials. Environ. Toxicol. Chem. 2010;29:715–721. © 2009 SETAC

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INTRODUCTION

Scientists from a variety of fields ranging from toxicology to environmental engineering to cell biology are investigating the environmental and health implications of nanomaterials [1–4]. These studies are addressing important issues related to the environmental, health, and safety (EHS) of nanomaterials. In many of these studies, nanomaterials are purchased from a commercial source. It is typical for the manufacturer to provide information on the chemical composition (e.g., TiO_2, Al_2O_3, Ag), phase, and size of the nanoparticles and there is often no independent characterization to verify this information. Therefore, the only characterization of these materials is that provided by the manufacturer. Furthermore, in many of these studies, only one source and one size of nanoparticles are used.

Two aspects of this approach are of concern. First, it is important, and in fact critical, that there be independent characterization of the nanomaterial given that there currently exist no industrial standards for characterizing nanoscale materials. The first point is the focus of the present study. Second, generalizing too much about nanoparticle behavior if there is no systematic study of size and the use of only one batch of nanoparticles from one company to generalize about all nanoparticle behavior should be done with caution.

The present study shows the information provided by the manufacturer may be incomplete and nonrepresentative of the entire sample and, in some cases, the data provided are incorrect. There are several reasons for this problem. One reason is that nanomaterials can be inhomogeneous and unlike molecules with exact formulae, nanomaterials are typically made up of a sample that contains a distribution of sizes. In addition, there are no standard methods for measuring properties such as particle size and surface area; thus different methods are used to report these physical properties, some of which are more accurate than others. In fact, much of the equipment needed to characterize nanoscale materials is expensive and/or specialized and therefore not readily available. This is especially true for small startup companies. Furthermore, there is batch-to-batch variability in the manufacturing of nanomaterials and not all batches are characterized. Therefore, it is important that independent characterization of commercially manufactured materials be performed in EHS studies of nanomaterials if the results are to be of use to the scientific community. The present study shows characterization data for three different commercially manufactured materials, including aluminum oxide nanoparticles, aluminum nanoparticles, and aluminum oxide nanowhiskers. There are clear discrepancies observed between the information provided by the manufacturer and the characterization data measured in this study using techniques and methods commonly used in academic research laboratories. Three examples are provided, and for all three differences are observed. In addition to the characterization data, a summary of some of the methods used in industry for nanomaterials characterization is discussed.

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Table 1. Nanomaterials used and the manufacturers' specifications[a]

Source	Composition (phase)	Size (nm)	Surface area (m^2/g) [b]	Shape
Sigma-Aldrich	Al_2O_3 (gamma)	< 50	> 40	Spheres
Nanostructured and amorphous materials	Al (fcc)	18	40–60	Spheres
Sigma-Aldrich	Al_2O_3	2–4	350–750 [c]	Whiskers

[a] Only data reported by the manufacturer is given in this table.
[b] Based on geometric area calculation.
[c] Value recently changed to approximately 155 m^2/g by the manufacturer based on the assumption of nanowhisker aggregation.

EXPERIMENTAL METHODS

The materials investigated include aluminum oxide nanoparticles, aluminum nanoparticles, and aluminum oxide nanowhiskers. These nanomaterials were purchased from commercial sources. Table 1 lists the sources of these materials and the properties of these source materials provided by the manufacturer. The characterization data provided by the manufacturer includes chemical composition, phase, particle size, and morphology, as well as surface area in some cases. This section describes some of the independent characterization methods used to get basic information on commercially manufactured nanomaterials that include characterization of the bulk phase of the nanomaterials and size (size-distribution) of the nanomaterials.

Powder X-ray diffraction

Powder X-ray diffraction (XRD) is used to identify crystal phase. XRD analysis was performed using a MiniFlex II X-ray diffractometer (Rigaku). A nonmonochromatic Co radiation source with an iron foil Kβ filter was used. The instrument was operated at 30 kV and 15 mA; a dwell time of 1 s per each angle with steps of 0.02°. The XRD patterns were converted to Cu Kα-based patterns to easily compare with corresponding patterns from the JCP2 database (provided by Bruker) and the American Mineralogist Crystal Structure database (AMCSD) [5].

Electron microscopy

Electron microscopy, both transmission and scanning electron microscopy, was used to investigate particle size and morphology. Transmission electron microscopy (TEM) images were obtained using a JEOL 1230 transmission electron microscope operated at 120 kV and 10 μA beam current. A Hitachi S-4800 scanning electron microscope was used to get scanning electron microscopy (SEM) images using a beam energy and current of 6 kV and 7 A, respectively. The images were processed using Image J software program, a Java-based public domain program (National Institutes of Health). For most analyses, each sample was dispersed in methanol and sonicated for 1 h to break possible agglomerates into individual particles so that the primary particle size distribution could be more easily determined. There is no evidence in our studies that show that this changes the properties of these nanomaterials, but it should be noted that sample preparation should be clearly stated, because it may play a role in nanomaterial characterization. The colloidal suspension was deposited onto the copper grid for TEM analysis and dried out for at least one day. Samples were prepared for SEM analysis in a similar manner as for TEM, except that an aluminum stub was used instead of the copper grid.

Brunauer, Emmett, and Teller specific surface area

Because an important property of nanomaterials is the high surface to volume ratio, surface area of nanomaterials is an important property that is often needed in nanomaterials characterization. In the present study, the Brunauer, Emmett, and Teller (BET) specific surface area (SSA) analysis was conducted using a Quantachrome BET Nova 4200e automated system. Nitrogen was used as the adsorbate at 77.4 K under isothermal conditions. Aluminum oxide nanoparticles were degassed at 120°C for 16 h, and aluminum and aluminum oxide nanowhiskers were degassed at 200°C for 1 d and 300°C for 5 h under vacuum before analysis. The analysis is typically based on a 7-point BET analysis.

RESULTS AND DISCUSSION

Below, three examples are presented for aluminum-based nanomaterials that demonstrate some of the important needs for independent characterization. This is, of course, a very small sample size and as such should be recognized as more of a presentation of case studies than a statistical analysis of manufactured nanomaterial characterization.

Independent characterization of commercially manufactured nanomaterials

Aluminum oxide nanoparticles. The characterization data for aluminum oxide, Al_2O_3, nanoparticles are shown in Figures 1 and 2. The XRD pattern in Figure 1 provides information on phase and composition for this crystalline material. Although the material is sold as gamma aluminum oxide (γ-Al_2O_3), the XRD pattern shows there is more than one phase present in the aluminum oxide sample. It is observed that several of the peaks do in fact match that expected for γ-Al_2O_3. In addition to the XRD peaks associated with γ-Al_2O_3, other XRD peaks are observed indicating other phases are present in the sample. These additional features appear in the range of 2θ between 25 to 30°, 40 to 45°, and 54 to 60°. These peaks match well with the XRD pattern for delta aluminum oxide (δ-Al_2O_3) as seen when compared with JCP 2 pattern number 04-0877 for δ-Al_2O_3. Delta and gamma aluminum oxides are known as metastable phases, possibly formed in the process of conversion from boehmite to the most stable aluminum oxide phase, alpha aluminum oxide (α-Al_2O_3), during calcination [6]. In the process of thermal decomposition with increasing temperature, γ-Al_2O_3 is formed before δ-Al_2O_3 and in a certain range of temperature, both phases coexist [6–9].

Figure 2 shows the TEM (Fig. 2A) and SEM (Fig. 2C) images obtained for this aluminum oxide sample. It can be seen in these images that the particles are nearly perfect solid spheres. The morphology seen in the images agrees well with

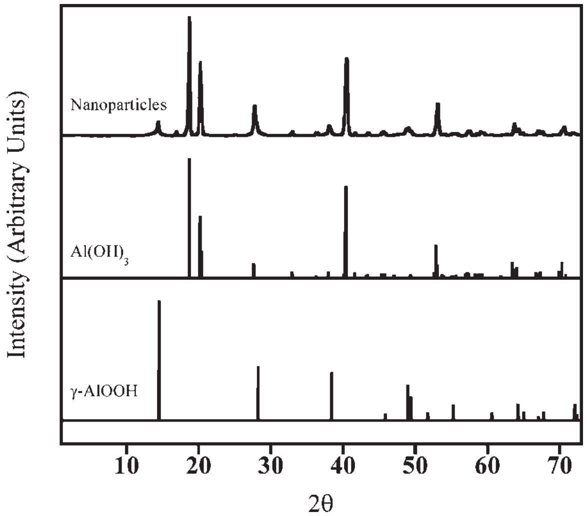

Fig. 1. X-ray diffraction (XRD) pattern of purchased commercial aluminum oxide nanoparticles compared with standard reference data for two aluminum oxide phases δ-Al_2O_3 and γ-Al_2O_3. The XRD pattern shows two phases present in the sample.

the manufacturer's description of these as particles as spherical. However, it is apparent that there is a distribution of sizes and the aluminum oxide sample is highly polydispersed. Polydispersity of particle size could be a result of rapid growth during the synthesis, with particle growth and nucleation occurring simultaneously [10]. In addition, the various particle sizes present in this sample may also be related to the fact that there are two phases present. Karthikeyan et al. [11] reported that δ-Al_2O_3 becomes larger in size than γ-Al_2O_3 during the synthetic process using flame spray, because the delta phase is formed at a higher temperature and more likely to fuse to be aggregates.

The size distribution histogram plotted in Figure 2B is based on the measurement of particle diameters for 200 particles from the TEM image. The histogram shows a broad size range. The particle sizes vary from 6 to 145 nm, and the average size and the standard deviation of the particles are 37 and 25, respectively. Even though the size of the most abundant particles is centered between 15 and 20 nm, the mean size is much larger, due to the presence of relatively large particles that are in the size range of a few hundred nanometers. Likewise, the

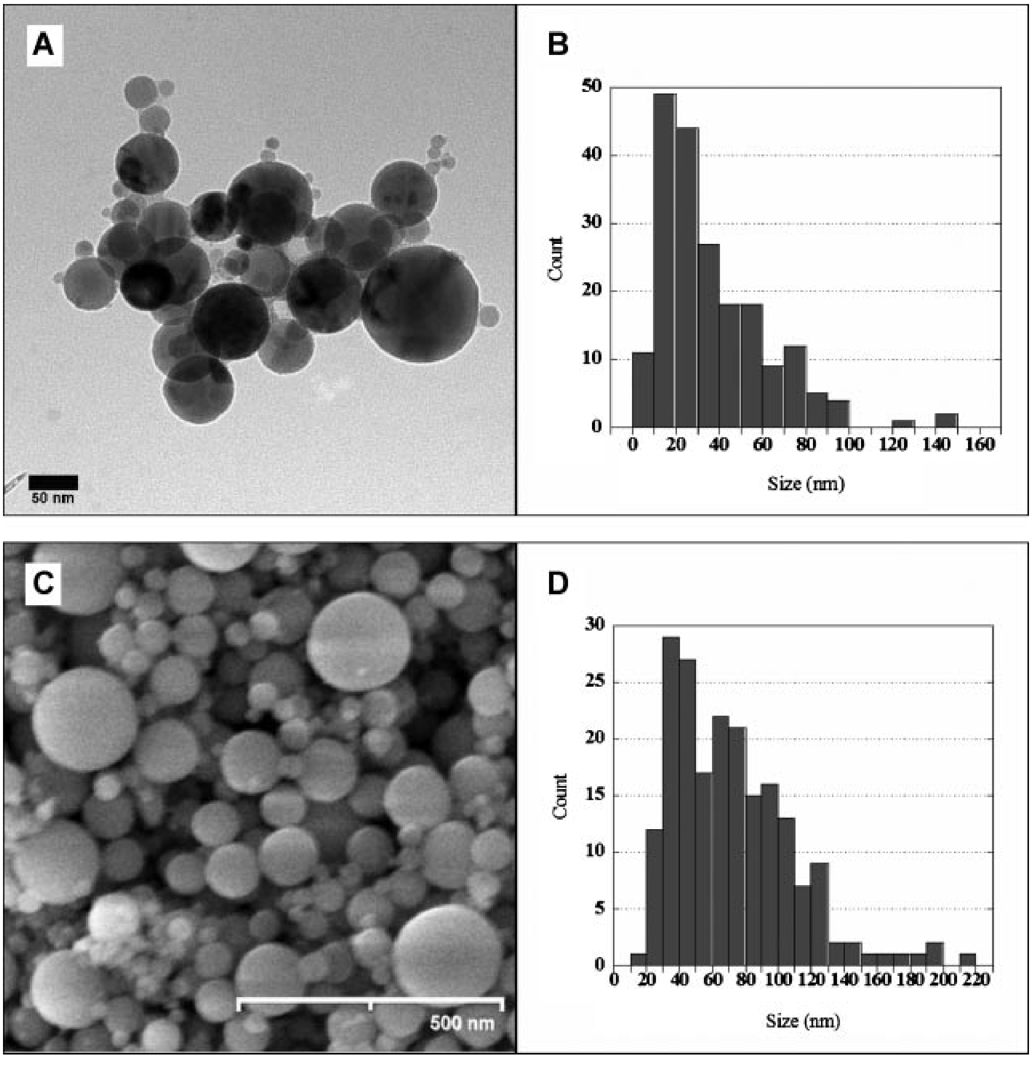

Fig. 2. (**A**) Transmission electron microscopy (TEM) images of commercial aluminum oxide nanoparticles. (**B**) Size distribution obtained from TEM images. (**C**) Scanning electron microscopy (SEM) image of commercial aluminum oxide nanoparticles. (**D**) Size distribution from SEM image. These images show that the sample is polydisperse. See text for further details.

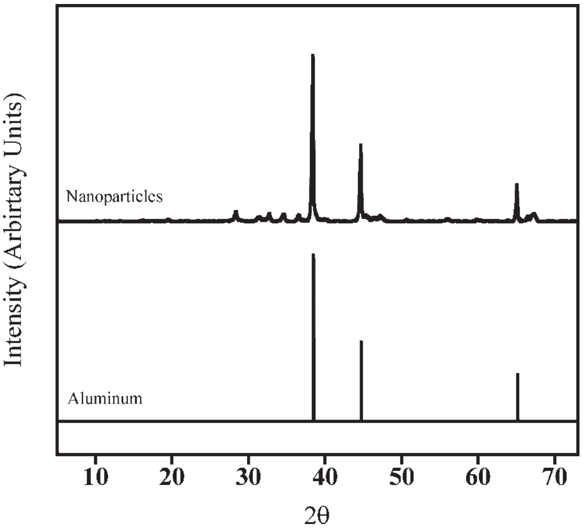

Fig. 3. X-ray diffraction (XRD) pattern of purchased commercial aluminum nanoparticles compared with standard reference data for aluminum metal (fcc structure). The XRD pattern shows that besides metallic aluminum there are also other diffraction peaks. These are most likely associated with an oxide phase (see Figure 1).

particle size histogram based on the SEM image shows a broad particle size distribution (Fig. 2D). However, the distribution is shifted to even larger size compared with that based on TEM, and most particles are in the range of 30 to 40 nm. The mean size is 72 ± 37 nm. The result of particle mean size is bigger in the SEM-based measurement may be related to how the particles pack. Particles on the top layer were only used to measure size.

As already noted, surface area is an important property of nanomaterials. The SSA of the aluminum oxide sample from seven-point BET analysis was determined to be $26 \pm 1\ m^2/g$. The average and standard deviation were obtained by triplicate measurements. This measurement is lower by 48% from that reported by the manufacturer.

Aluminum nanoparticles. The XRD pattern of the sample matches well that for aluminum metal which crystallizes in a cubic close packed structure (Fig. 3). Additional reflections are seen in the 2θ range of 28 to 38° with reflections at 44.8 and 65.2°. These are most likely associated with an oxide layer. Without coatings or organic surface functionalization to passivate the reactivity of the aluminum metal surface,

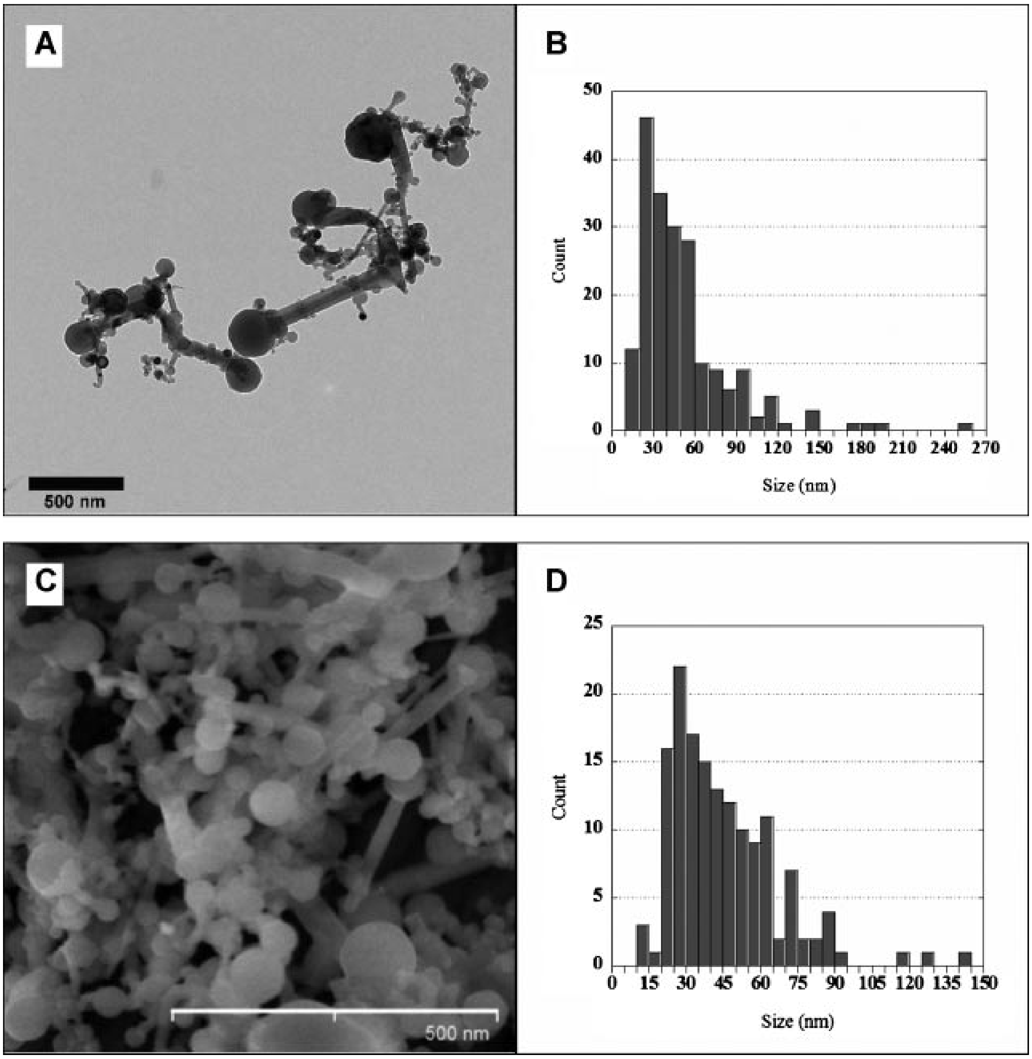

Fig. 4. (**A**) Transmission electron microscopy (TEM) images of commercial aluminum nanoparticles. (**B**) Size distribution obtained for spherical particles from TEM images. (**C**) Scanning electron microscopy (SEM) image of commercial aluminum oxide nanoparticles. (**D**) Size distribution for spherical particles from SEM image. These images show that the sample is of mixed morphology. See text for further details.

oxidation can readily occur. For small size aluminum nanoparticles, the surface rapidly reacts with oxygen from air under ambient conditions [12–18]. The oxide phase is characterized as a mixture of gamma and delta aluminum oxide, as they agree well with the reference patterns shown for these aluminum oxide phases in Figure 1. The oxide phase is considered to be more than 1 to 2 w% composition or greater than approximately 2-nm-thick coating according to the XRD detection limit [19]. X-ray photoelectron spectroscopy analysis, a surface sensitive technique, was also performed to verify the aluminum oxide components on the surface. This experiment is not described in detail here.

Transmission electron microscopy and SEM images (Fig. 4) reveal interesting and important information on particle size and shape. The images clearly show particles with spherical shapes in agreement with the manufacturer's description of these as spherical particles. However, there are also particles with quite different shapes in the sample resembling metal tubes or bars, some of which look connected with spherical particles, resembling a dumbbell shape. These particles clearly have very different morphologies than spherical, which is the description provided by the manufacturer. It is supposed that in the manufacturing process, this rod-shaped aluminum was produced as a byproduct. It is known that the quality of a catalyst and different concentrations of a surface passivation agent can give rise to nonhomogeneously distributed aluminum nanoparticle product. Furthermore, different morphologies, such as elongated structures, can be produced in wet chemical synthesis of aluminum nanoparticles [12].

For the spherical particles, the most abundant particle size is in the range of 20 to 30 nm, as shown by the peak in the histogram in Figure 4B, but the average particle size is 51 ± 35 nm based on the measurement of 200 particles. A long tail to larger particle size is clearly shown in the histogram; thus the much greater average particle size and the large standard deviation. The size distribution based on the SEM image (Fig. 4D) shows a similar result as shown in the size distribution based on the TEM image. The majority of particles are 25 to 30 nm and the average particle size results in 45 ± 22 by measuring 150 particle sizes.

The SSA of the sample is 23 ± 1 m^2/g based on 7-point BET analysis. The manufacturer reports 40 to 60 m^2/g and TEM image of this sample provided by the company shows no rods connecting spheres. Thus, the inconsistency in the surface areas between independent measurement and the analysis from the company is considered to potentially be due to batch-to-batch differences in sample production.

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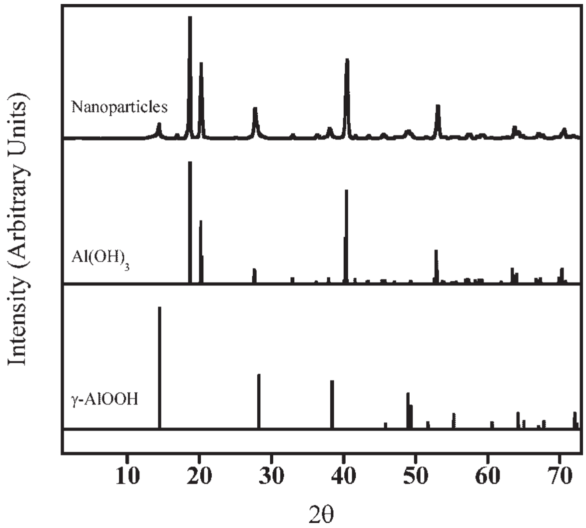

Fig. 5. X-ray diffraction (XRD) pattern of purchased commercial aluminum oxide (Al_2O_3, according to the manufacturer) nanowhiskers compared with standard reference data. Because the XRD pattern did not match any of the known XRD patterns for various aluminum oxide phases (α, η, γ, and δ) the X-ray database was further searched. The middle and bottom XRD patterns are of hydroxy and oxy(hydroxy) phases, $Al(OH)_3$ and γ-AlOOH, respectively. From these reference data, the XRD pattern of the commercial nanowhiskers can be seen to contain a mixture of $Al(OH)_3$ and γ-AlOOH. See text for further detail.

Aluminum oxide nanowhiskers. Aluminum oxide nanowhiskers were characterized with XRD as shown in Figure 5. The manufacturer's stated formula for the nanowhiskers is Al_2O_3. Although attempts were made to match the XRD pattern of the nanowhiskers with any of the known aluminum oxide phases (γ, δ, η, and α), these attempts were unsuccessful. Instead the XRD pattern of the aluminum oxide nanowhiskers align well with the XRD patterns of aluminum hydroxides and aluminum oxyhydroxides, including bayerite, $Al(OH)_3$, and boehmite, γ-AlOOH. Thus, in this case even the chemical formula reported by the manufacturer is not correct. Based on the XRD patterns, it appears that the aluminum oxide nanowhiskers are a mixture of bayerite and boehmite, with bayerite being the major component with chemical formula as noted above of $Al(OH)_3$.

It is somewhat difficult to observe discrete individual whiskers in the TEM and SEM images (Fig. 5). This is partly due to the fact that the sample is extremely hygroscopic and easily aggregates. In the SEM image, the aggregate appears as floccus but in the TEM image, fibers are more easily observed, somewhat resembling other nanomaterial fibers such as carbon nanotubes. The length of each whisker is not very clear from the image. Hence, only widths of whiskers are used to obtain average size and size distribution. As it is shown in Figure 6B, the size distribution is narrow and its average width is 3 ± 0.6 nm based on the measurement of 100 fibers. Most particle shapes from TEM images are flake and whisker shapes, and the crystal morphology of bayerite is very fine fibers and also flaky and tabular shaped. Consistent with the XRD results that the sample contains bayerite as its majority component.

The SSA of the sample was obtained to be 273 ± 5 m^2/g based on the seven-point BET analysis method. However, the result is a negative BET constant and a y intercept in the range of p/p_0, 0.05 to 0.3 where BET isotherm is nearly linear. Thus, linear regression of BET isotherm was recalculated in the nitrogen partial pressure (p/p_0) range, 0.05 to 0.1 where the isotherm is the most linear and its y intercept is a positive value. Based on that modification, the SSA of this sample was calculated to be 320 ± 4 m^2/g.

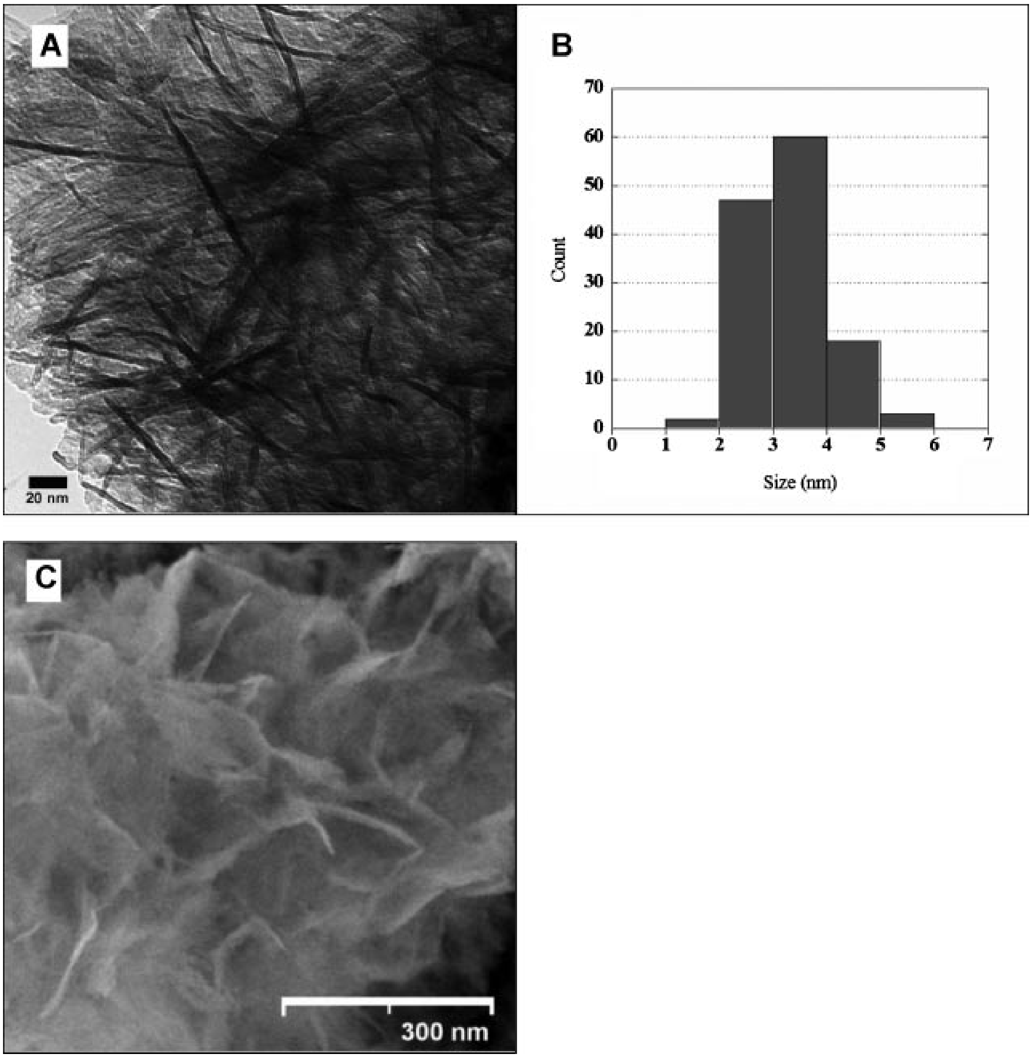

Fig. 6. (**A**) Transmission electron microscopy (TEM) images of commercial aluminum oxide nanowhiskers. (**B**) Size distribution of the widths of aluminum oxide nanowhiskers based on TEM image. (**C**) Scanning electron microscopy (SEM) image of commercial aluminum oxide nanowhiskers. It is hard to extract information about size from the SEM image so no histogram is reported. See text for further details.

Methods used to characterize manufactured nanomaterials. As shown above, independent characterization differs from what is provided by the manufacturer. It is important to know what methods are being used to characterize manufactured nanomaterials, and to realize that companies often do not have access to the state-of-the-art methods used in academic research laboratories.

For crystalline materials, companies use X-ray diffraction techniques that yield chemical composition and phase information. However, amorphous phases are not well characterized with this technique. In addition, there may not be a powder XRD analysis for every batch.

If one considers particle size, there are various analytical techniques for measuring the size of nanoparticles. It has been suggested that the categories for different techniques can be broadly divided into two, behavioral techniques and direct observation [20,21]. These categories indicate that the measurement is carried out in situ and ex situ for the former and the latter, respectively. Dynamic light scattering, scanning mobility particle sizer, and aerodynamic particle sizer are in the former category. These measurements are good for spherical particles and may not be useful for certain samples. Also, they are not always readily available in industry. Measurement techniques of particle size based on microscopy techniques such as TEM, SEM, and atomic force microscopy are also expensive. These methods provide information about primary particle size [20,22]. Because some of these methods are not readily available, alternative techniques are often used to get a particle size. For example, through XRD, a particle size can be calculated using Scherer's equation and diffraction line widths, but these provide only a rough value because all particles in a sample are not considered in the calculations and the calculations assume monodispersed samples. From this analysis geometric surface areas are typically calculated. Thus, a problem develops where one parameter is calculated from another parameter that is perhaps not determined using the best methods available. Therefore, data would be over-analyzed, especially for nanoparticle size measurements.

CONCLUSIONS AND IMPLICATIONS OF THESE STUDIES

There were significant differences between independent characterization data and information provided by the manufacturer for purchased nanomaterials. This is most likely a result of a lack of standards for sample measurements, methods and protocols, and, potentially, batch-to-batch variability. In these studies we have shown that samples can be highly polydispersed and thus conclusions drawn in EHS studies using polydispersed samples may lead to erroneous conclusions on the hazards and risks of a particular nanoparticle size. It is also shown here that particles may contain mixed morphologies. Given that there are many questions as to the importance of particle morphology on the hazards and risks of manufactured nanomaterials, the fact that particles of high aspect ratio are mixed in with spherical particles raises questions about what conclusions can be drawn about samples that contain these mixtures. A minority component, e.g., rod-like or dumbbell-shaped particles that are present, may yield a type of result that differs from the majority component, e.g., spherical particles. Thus, conclusions drawn about a sample that contains mixed morphologies, especially when that information is unknown, may be in error. In addition, it is shown that particle phase and composition reported by the company can, in fact, be incorrect. This in turn means that conclusions drawn by EHS researchers may again be erroneous given that the results reported are actually for a very different type of nanomaterial. Thus a major conclusion that has come about from this current study is that independent characterizations of commercial materials are an important and necessary component of the study design. It should also be noted that not all important and relevant nanomaterial properties were investigated here. In particular, given the importance of surface composition and surface functionality, it may be appropriate to have methods for surface chemical characterization as a component of the study design.

Furthermore, established standard methods for the measurement of nanoparticle properties are needed in order for the field of environmental and health implications of these materials to be fully recognized and correlated to nanomaterial properties. These measurements should be performed not only of the materials themselves in powder form, but also in the environment that is of interest, whether it be in natural water systems or in vivo, as described in the MINChar initiative (Minimum Information for Nanomaterial Characterization Initiative: Supporting Appropriate Material Characterization in Nano-toxicology Studies, http://characterizationmatters.org) and in recent editorials [4,23] and reviews [24].

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