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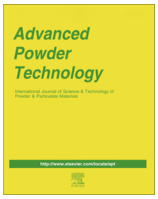

Original Research Paper

# Size and shape distributions of primary crystallites in titania aggregates

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ABSTRACT

The primary crystallite size of titania powder relates to its properties in a number of applications. Transmission electron microscopy was used in this interlaboratory comparison (ILC) to measure primary crystallite size and shape distributions for a commercial aggregated titania powder. Data of four size descriptors and two shape descriptors were evaluated across nine laboratories. Data repeatability and reproducibility was evaluated by analysis of variance. One-third of the laboratory pairs had similar size descriptor data, but 83% of the pairs had similar aspect ratio data. Scale descriptor distributions were generally unimodal and were well-described by lognormal reference models. Shape descriptor distributions were multi-modal but data visualization plots demonstrated that the Weibull distribution was preferred to the normal distribution. For the equivalent circular diameter size descriptor, measurement uncertainties of the lognormal distribution scale and width parameters were 9.5% and 22%, respectively. For the aspect ratio shape descriptor, the measurement uncertainties of the Weibull distribution scale and width parameters were 7.0% and 26%, respectively. Both measurement uncertainty estimates and data visualizations should be used to analyze size and shape distributions of particles on the nanoscale.

## 1. Introduction

This section reviews particle size and shape distributions by transmission electron microscopy (TEM), stakeholder needs for this information, morphology descriptions of powder aggregates, the relevance of primary crystallite size and shape distributions for titania applications, and the project objectives.

### *1.1. Size and shape distributions by transmission electron microscopy*

While many of the measurements methods for particle sizes in the nanoscale have focused on assessing an average particle size, the performance properties of nanoparticles often depend on size and shape distributions. Indeed, the nanoparticle size distribution is important to product performance in applications, in the environment, and for health, safety, and regulatory issues. Transmission electron microscopy (TEM) is a standard method for determining nanoparticle sizes.

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This case study provides a scientific foundation for an International Organization for Standardization (ISO; www.iso.org) standard for the measurement of particle size distributions on the nanoscale by TEM. The specific ISO committee is ISO/TC229 Nanotechnologies, which was formed in 2005 and has 34 national member bodies, ∼40 liaison members (other ISO technical committees or international organizations) and 11 observers. The authors of this study include members of Joint Working Group 2 (JWG2), Measurements and Methods. This particular project is a consensus choice of JWG2 as an example of aggregated particle size and shape distributions. ISO standards exist for the graphical representation of particle size distributions [1], calculation of average size and moments [2], fitting reference models to distribution data [3], logarithmic normal probability distributions [4], descriptors for particle size and shape [5], accuracy of measurement methods [6,7], and static image analysis methods [8]. These methods have been applied to measurements made for this project. The interlaboratory comparison team includes four national metrology institutes, three titania manufacturing companies, two regulatory agencies, and a university.

Although transmission electron microscopy (TEM) has been extensively applied to characterize nanomaterials, standard methods for imaging, analyzing and reporting size distributions are lacking. Exceptions to this circumstance are the average particle sizes and the associated measurement uncertainties for TEM analyses of reference materials [9] and certificated reference materials [10]. Nanomaterial and nanoparticle products are moving toward, or are in, the marketplace. Commercial and regulatory stakeholders will need guidance on measurement methods and their measurement uncertainties when evaluated by multiple laboratories. Classical analysis methods are available for particle size and particle size uncertainties [11–14]. A semi-automated image analysis method has reported size distribution statistics from an interlaboratory comparison (ILC) [15] of gold reference material samples [9]. Here, a more realistic, commercial sample of nanoscale titanium dioxide in an aggregated/agglomerated state is analyzed using manual image analysis methods.

### 1.2. Stakeholder needs for size and shape distribution data

Size and shape distribution measurements and analyses of titania powders are needed by multiple stakeholders, e.g., academia, industry, government and the public at large. Titania powder performance properties have been related to their physico-chemical characteristics, including size, shape, surface structure and surface texture. In this work, the TEM measurements are not compared to traditional, one-point estimates for particle size, such as x-ray diffraction (XRD) or specific surface area (BET) analysis. Neither method, XRD or BET, can provide information about particle shape. Our methods report the primary crystallite size and shape distribution, estimate parameters of references distributions fitted to the data, compute measurement uncertainties of these parameters, and visualize the correspondence between the data and the fitted reference distributions.

This protocol was developed based on an interlaboratory comparison (ILC) study that conformed to guidelines established by the Versailles Project on Advanced Materials and Standards (VAMAS) [16] and ISO 5725 [17]. Key needs of the International Standards stakeholder and user community include: (1) measurement of ‘real life’ materials, (2) highly automated protocol steps, including image acquisition, particle capture, data quality assessments, (3) comparison of data to reference distribution models, (4) measurement uncertainty assessments for evaluations by different laboratories, and (5) data visualization tools to compare methods, procedures, and descriptors. JWG2 of ISO/TC229 has established five ILC case studies for a broad spectrum of particle types. These include: unimodal, discrete spheroidal nanoparticles (gold), a bimodal mixture of discrete nanoparticles (colloidal silicas), a discrete nanoparticle mixture with different shapes (gold nanorods), amorphous aciniform aggregates (carbon black), and aggregates of primary crystallites (titania). The protocol provides an example of determining size and shape descriptors by manually outlining aggregated primary crystallites with clearly defined edges [18]. The approach is based on methods reported for titania powder synthesis research plus methods in use by titanium dioxide manufacturers.

### 1.3. Morphologies of powder aggregates

A recent study [19] has helped identify differences of the internal morphologies of powder aggregates in the categories, amorphous (silica gel), paracrystalline (carbon black), crystalline and amorphous (siliceous earth and organic clay), amorphous shell over crystalline core (silica-coated titania), and crystalline aggregates (iron oxide, fumed alumina, calcium carbonate and titania). While the term, primary particle, has been used to describe the individual elements fused together in titania aggregates [20], ‘primary crystallite’ is a more precise term as there are grain boundaries between these elements [19].

### 1.4. Relevance of size and shape distributions for titania applications

Aggregate particle size distributions are frequently measured via non-microscopy methods, such as those that measure hydrodynamic particle size (e.g., centrifugal liquid sedimentation); these have been the subject of multiple interlaboratory comparisons in the past. Here, the focus is on the measurement of size and shape distributions of primary crystallites in a titanium dioxide sample. This titania was a commercial powder sample consisting of primary crystallites aggregated to micron-scale particles. The sizes and shapes of the primary crystallites are known to link with the performance of titania, as shown in Table 1. In many of these applications, the size and shape of the primay crystallites of the titania aggregate are essential to product performance rather than the size and shape of the aggregate. Titania’s primary crystallite size has been linked to its performance as a catalyst [21–25], as a photocatalyst [26,27], in photooxidation [28,29], and in cytotoxicity tests [30–32] [33]. Particle shape has also been linked to the performance of titania in optical applications [34–36]. Primary crystallite grain shapes vary and there have been recent reports of specific shapes affecting titania performance in new applications [37–39].

The primary crystallites of titania aggregates are tightly fused and it is not reasonable to use mechanical action to release primary crystallites for direct measurement [40]. In addition, as-manufactured titania products can have residual acidic or basic impurities on their surfaces [41] or surface coatings of some type. For use in consumer or commercial products, metal oxides are

**Table 1**
Titania applications dependent on primary crystallite size.

| Application | Preferred primary crystallite size, nm | Reference |
|---|---|---|
| Lithium ion electrodes | <1500 | [41] |
| Powder cosmetics | 25–200 | [42,43] |
| Nanocomposite fibers | 35 | [44] |
| Dye cell photoanodes | 50 | [45] |
| Photocatalysts | 20 | [46] |
| IR-reflective nanocomposites | 41 | [47] |
| Slurry polishing compound | 10–70 | [48] |
| Light emitting diodes | 30 | [49] |
| Conductive ceramics | <100 | [50] |

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