Journal of the Australian Ceramic Society Volume 44[2], 2008, 47-51

Assessment of Particle Sizing Methods Applied to Agglomerated Nanoscale Tin Oxide (SnO_2)

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Available Online at: www.austceram.com/ACS-Journal-2008vol2.asp

Abstract
Tin oxide (SnO_2) was obtained from the thermal decomposition of tin oxalate (SnC_2O_4) at 800°C for 1 h. The precursor was precipitated at room temperature from the reaction of aqueous solutions of 0.04 M tin (II) chloride and 0.04 M oxalic acid. X-ray diffraction data of the calcined powder showed that it consisted of high-purity tetragonal SnO_2. Examination using a field emission scanning electron microscopy (FESEM) showed that the individual particles were spherical in shape, with a mean diameter of ~75 nm. De-caking with a mortar and pestle of the calcined powders in the presence of atmospheric water vapour caused agglomeration. The agglomerate sizes were determined by four different techniques. They were assessed in terms of the mean diameters, which were calculated from the volume distribution data. Each instrument gave a different result: The main uncertainties with these data are associated with the non-spherical agglomerate shape, which caused three effects on the data provided by the instruments.

Plate face size variations resulted in multimodal size distributions; the non-spherical particle size is in contradiction to the particle shape assumed by the instruments; the non-spherical particle size resulted in non-Gaussian distribution peaks.

Keywords: Tin oxide, X-ray diffraction, electron microscopy, morphology, particle size, agglomeration

INTRODUCTION

The properties of a ceramic product depend on its processing route and the properties of the raw materials. Therefore, the characterisation of powders is one of the most important tools in assessing their properties. Such characterisation typically involves examination of the particle size, size distribution, and morphology [1]. By understanding the behavior and properties of powders, suitable processing procedures for the materials can be determined, thereby yielding desirable properties in the final product.

When producing powders in-house, it is particularly important to determine these particle characteristics. The most common methods of characterisation are sieving, electron microscopy, laser light diffraction, ultra- and disc-centrifugation, and electrical sensing zone methods [1–3]. Each of these methods has its own principles, advantages, disadvantages, and limitations. Therefore, choosing the right measurement method for particle size analysis is crucial in order to ensure that the particle size analysis results obtained are accurate. The accuracy of these data is important in making decisions concerning further powder processing.

The present work described particle sizing data obtained using four particle sizing instruments and tin oxide (SnO_2). The differences can be explained in terms of the (1) morphologies and sizes of the agglomerates, (2) basic operating principles of the instruments, (3) sample preparation for each analysis, and (4) limitations of each instrument.

EXPERIMENTAL PROCEDURE

Sample Preparation and Characterisation

Tin (II) chloride dihydrate (98 wt%, BDH, VWR International Ltd., Germany) and oxalic acid dihydrate (99.5 wt%, Ajax FineChem, Australia) were used as the starting materials. Aqueous solutions of 0.04 M concentration were prepared. The subsequent processing procedures were identical to those described elsewhere in the present volume [4].

Powders of the product SnO_2 were characterised in terms of mineralogy and morphology as described elsewhere in the present volume [4].

Particle Sizing Units

Particle size characterisation was done using four different techniques:

i) Zetasizer Nano (Malvern Instrument, UK)
ii) 90Plus Particle Size Analyzer (Brookhaven Instrument Corp., USA)
iii) Particle Counter 9064 (HIAC and ROYCO, USA)
iv) Coulter Counter LS230 (Coulter Corp., USA)

The agglomerate sizes determined consist of the mean diameters, which are derived from the volume distribution data.

RESULTS AND DISCUSSION

Phase Analysis

As shown in Figure 1, the calcined powder consisted of single-phase, well crystallised tetragonal SnO_2.

Particle Size and Agglomerate Morphology

As shown in Figure 2, FESEM micrograph showed that the SnO_2 consisted of spherical particles of consistent ~75 nm diameter. It also can be seen that the particles were agglomerated, which resulted from (1) atmospheric water adsorption, (2) onset of tackiness, (3) laminar flow under the action of grinding by mortar and pestle, and (4) the formation of platy laminates [4].

Agglomerate Size

The use of electron microscopy generates what is known as a *number-length mean*, which also is known as D[1,0]. Although this is a direct visual method of assessment, it is limited to a two-dimensional analysis that gives an image of the diameter [5]. In contrast, other particle sizing techniques, which are, by necessity, indirect, use other parameters to calculate the means. These methods use the surface area to calculate the *surface-moment mean* (D[3,2]) and the volume to calculate the *volume-moment mean* (D[4,3]).

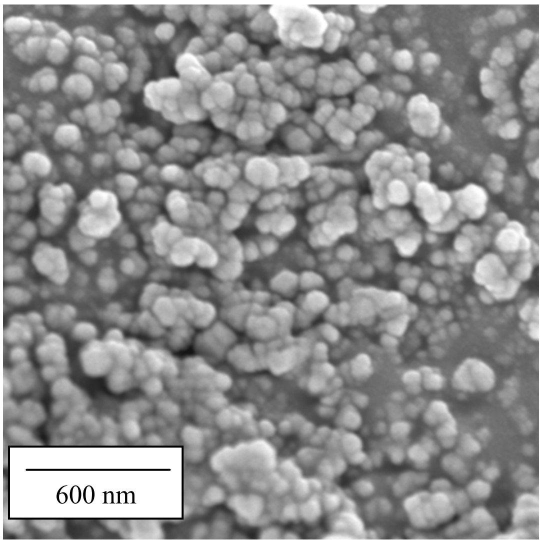

Figure 2: FESEM micrograph of the SnO_2 powder

Since the sizing data did not indicate any distribution peaks corresponding to ~75 nm, it is clear that the units, which rely on optical means of analysis, measured the agglomerate size and not the particle size. This type of observation emphasises the importance of inspecting the actual size characteristics by direct means, such as FESEM, rather than to rely solely on indirect means, *viz.*, particle sizing methods.

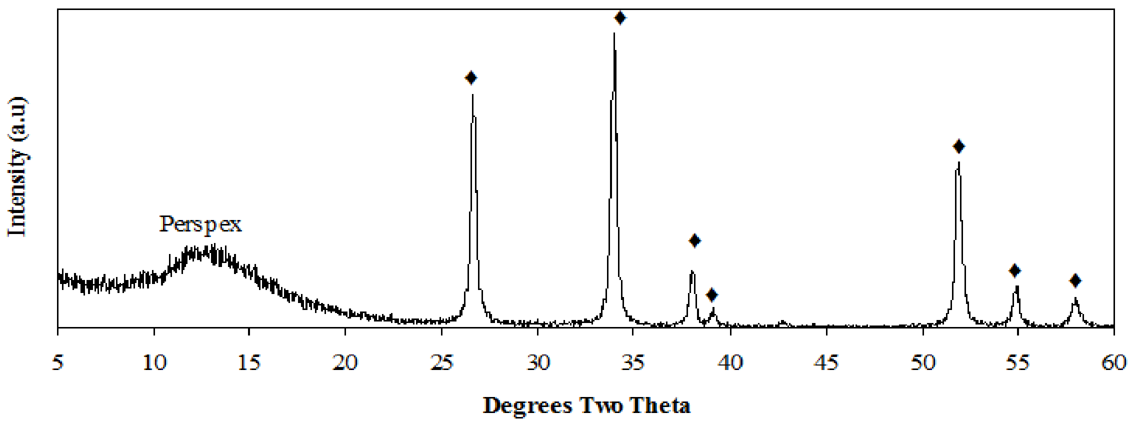

Figure 1: X-ray diffraction pattern of the SnO_2 powder (♦ = SnO_2)

Particle Sizing Principles

The main differences between the four particle sizing techniques used are outlined in Table 1 on the following page.

Dynamic Light Scattering

The Zetasizer Nano and the 90Plus Particle Size Analyzer use the dynamic light scattering principle, which also is known as photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS). With these two instruments, a laser beam is directed at a suspension, in which suspended particles move in Brownian motion. Light scattered by the moving particles gives rise to interference, which affects the intensity sensed by the detector. Analysis of the intensity gives the diffusion coefficient of the particles. The diffusion coefficient, viscosity, and temperature are used in the Stokes-Einstein equation to obtain the hydrodynamic diameter of the particles [6,7].

Forward Light Scattering

The Particle Counter 9064 consists of three main parts: sensor, sampler cell, and particle counter. Detection of the particles by the sensor is achieved using near-forward light scattering. Electrical pulses are generated whenever the particles in the sampler cell scatter the laser light and alter the intensity detected by a photodiode. The particle size is determined based on the proportionality of the amplitude of the pulses to the light intensity. The number and intensity of the pulses are used by the particle counter to determine the number fraction [8].

The Coulter Counter LS230 uses a similar principle. Samples are dispersed in a fluid module with the help of a sonifier installed in the unit. The particles diffract the laser light that is directed through the cell. The scattered light then is detected and collected by a sensor to obtain the distribution of the particles [9].

For all four units, the particle sizes obtained are recorded as mean diameters using volume distribution data.

Particle Sizing Data

Table 1 and 2 gives the results for the particle size analyses using the four units. The means and standard deviations are indicative only because these data are based on the peak for the smallest agglomerate size, which also represented the major distribution peak of each analysis, all of which were bimodal or trimodal. The main distribution peaks were not symmetric and thus non-Gaussian.

Table 1: Mean agglomerate diameters

Instrument	Mean Diameter (μm)
ZetaSizer Nano	0.295 ± 0.143
90Plus Particle Size Analyzer	0.532 ± 0.048
Particle Counter 9064	1.050 ± 0.480
Coulter Counter LS230	1.848 ± 0.706

The conclusions that can be made from these data are the two lowest values are somewhat close, possibly because the same operating principles were used for these units. The smallest size is likely to be a result of the fact that the wide scattering angle of this unit favours detection of small particles.

In addition to these limited comments, some other conclusions are possible due to the non-spherical nature of the platy agglomerates is likely to explain the main bimodal distribution peaks since the aspect ratio is very high. The Zetasizer Nano and Coulter Counter LS230 yielded bimodal distributions.

The likelihood of thickness variations of the platy agglomerates, which was not assessed with the FESEM, may explain the trimodal distributions. The 90Plus Particle Size Analyzer and the Particle Counter 9064 yielded trimodal distributions.The preceding comments allow the inference that the distribution peak of the larger size would correspond to the plate's face while that of the smaller size would correspond to the plate's edge. Therefore, according to volume considerations, the particle distribution peaks should consist of a large peak at the larger size (face) and a smaller peak at the smaller size (edge). This is the converse of the results, which show that the largest peak corresponded to the smallest size. Therefore, the preceding scenarios cannot be correct.

Consequently, the multimodal distributions are likely to reflect solely the sizes of the faces of the platy agglomerates, where there were some large outliers that, while few in number, appeared to the units as being of large volume.The variations in mean diameter cannot be attributed to settling effects since all of the values are <2 μm, which is adequate for colloidal suspension.

Ultimately, the mean diameters remain uncertain as a result of their non-spherical shape, which are not the morphology for which the units were designed and which are known to be problematic [12].

SUMMARY

There are significant differences in the apparent agglomerate sizes obtained using the four measuring techniques. Substantial differences were observed even for data obtained from techniques based on the same operating principles. It is likely that the main reason for these inconsistencies is simply the nature of the non-spherical agglomerates, the morphology of which the sizing units were not designed. The multimodal distributions are likely to have resulted from size variations in the plate faces rather than being a result of the aspect ratio of the platy agglomerates.

Table 2: Comparison between particle sizing techniques

Instrument	ZetaSizer Nano	90Plus Particle Size Analyzer	Particle Counter 9064	Coulter Counter LS 230
General principles employed	• Dynamic light scattering • Photon correlation Spectroscopy • Measures the intensity fluctuations of scattered light arising from the Brownian motion of particles • Backscattered detection at 173^o	• Dynamic light scattering • Measures scattering angle at 90^o or 15^o • Measures the intensity fluctuations of scattered light arising from the Brownian motion of particles	• Near-forward light scattering	• Forward light scattering • PIDS (polarization intensity differential scattering)
Particle size range	0.1 nm to 10 µm	0.5 nm to 5 µm	0.5 µm to 350 µm	0.04 µm to 2000 µm
Sample preparation				
• Suspension	Distilled water and 10 mM NaCl	Distilled water	Distilled water	Tap Water
• Volume of suspension	~3 mL	~3 mL	~10 mL	~12 mL
• Suspension concentration	0.003 vol%	0.003 vol%	0.001 vol%	0.3 vol%
Sonification during analysis	No	No	No	Yes
Instrument limitations	• Requirement of a dilute sample suspension. • Sensistivity greater for smaller particles, which means that that data favour small particles. • Particle shape affects the movement of particles in suspension, thereby affecting Brownian motion [10,11].	• Requirement of a dilute sample suspension; multiple scattering from particles may occur if suspension is concentrated. • Particle shape affects the movement of particles in suspension, thereby affecting Brownian motion [10,11].	• Requirement of a very dilute sample suspension. • Sensitivity to dust and even to water particles is high, so the result obtained may include data for water and/or dust particles.	• Instrument may be set up with tap water, which can cause bubbling from degassing during water temperature increase; bubble size range may be ~100-500 µm and elimination by background measurement is not possible [9].

ACKNOWLEDGEMENT

The authors would like to thank the Universiti Tun Hussein Onn Malaysia (UTHM) and the Ministry of Higher Education, Malaysia, for financial support for this work.

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