PARTICLE SIZE CHARACTERIZATION OF NANOPARTICLES – A PRACTICAL APPROACH

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Abstract: *Most properties of nanoparticles are size-dependent. In fact, the novel properties of nanoaprticles do not prevail until the size has been reduced to the nanometer scale. The particle size and size distribution of alumina nanoparticle, as a critical properties, have been determined by transmission electron microscopy (TEM), photon correlation spectroscopy (PCS), surface area analysis (BET) and x-ray diffraction peak broadening analysis. The particle size was found to be in the range of 5-95nm. Cumulative percentage frequency plot of the data extracted form TEM images indicates that particle size distribution obeys the log-normal function. The TEM images also reveal that particles are spherical in shape and loosely agglomerated. Comparing of the XRD and TEM results shows that the particles are single-crystal. The HRTEM images also verify that the particles have a single-crystal nature. In comparison, there is a good correlation between the BET, XRD and TEM measurements other than PCS that is sensitive to the presence of the agglomerates.*

Keywords: *Particle size, Alumina, Nanoparticles, TEM, XRD, BET, PCS*

1. INTRODUCTION

Nanoparticles and nanoparticle-based devices are of interest in numerous industrial applications due to their unique and often advantageous properties. The high surface-to-volume ratio together with size effects (quantum effects) of nanoparticles introduces many size-dependent phenomena such as chemical, electronic, magnetic and mechanical properties. For example, the melting point of nanoparticles is evidently decreased when the size is reached to the nanometer scale [1, ¬2]. The particle size plays a crucial role in nanoparticle properties and therefore an essential task in property characterization of nanoparticles is particle sizing.

The particle size and size distribution of nanoparticles can be determined using numerous commercially available instruments. Instruments can be used for the analysis of dry powders and powders dispersed in suspension.

In general, there are two basic methods of defining particle size. The first method is to inspect the particles and make actual measurements of their dimensions. Microscopic techniques, for example, measure many dimensional parameters from particle images. The second method utilizes the relationship between particle behavior and its size. This often implies an assumption of equivalent spherical size developed using a size-dependent property of the particle and relating it to a linear dimension [3]. Equivalent spherical diameters are the diameters of spheres that have the same or equivalent length, volume and etc. as irregular particles themselves. An example of this method is photon correlation spectroscopy (PCS) that the dynamic fluctuation of the scattered light intensity is the basis for calculation of the average particle size [4]. It is not possible to discuss rationally the size of a particle without considering the three-dimensional characteristics (shape) of the particle itself. This is because the size of a particle is expressed either in terms of linear dimension characteristics derived from its shape or in terms of its projected surface or volume. On the other hand, because the particles being studied are not the exact same size, information is required about the average particle size and the distribution of sizes about that average.

Additionally, by comparing the results from different instruments with each other, one can obtain extra information about the system. For example, ratio of the median diameter from PCS

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and the d_{BET} can be defined as the agglomeration factor F_{AG} indicative of the state of agglomeration of the nanoaprticles [4, 5].

Some studies were concerned with the particle sizing of nanoparticles. In a study by Staiger et al., particle size of alumina nanoparticles has been measured and an assessment of agglomeration of the nanoparticles has been done using the results [4]. Bowen has obtained particle size distribution of ceramic nanoparticles using different instrument from nanometer to millimeter [6]. In a study, Rawle has measured the particle size of barium ferrite nanoparticles by surface area analysis and laser diffraction. The different interpretations of the results have been discussed and shown the nanopowders are collections of micron-sized (agglomerates and aggregates) which simultaneously exhibit both nano and micron-based properties [7].

In this study, the different techniques include transmission electron microscopy (TEM), photon correlation spectroscopy (PCS), surface area analysis (BET) and x-ray diffraction peak broadening analysis have been used to characterize the particle size of plasma-synthesized alumina nanoparticles. The capabilities and limitations of these techniques are examined, together with a brief description of the general principles on which these methods are based.

2. EXPERIMENTAL PROCEDURE

Alumina nanoparticles were prepared in a DC plasma reactor (Plasma Technik, Swiss). In this technique, Aluminum metal powder with the average size of 45µm was injected into the plasma jet. The powder particles melt and vaporize and the molten droplets and vapors of aluminum react with oxygen resulting in the formation of aluminum oxide. The subsequent rapid quenching of the system results in producing nano-sized particles. The resulting product is a nano-sized white powder. The high-resolution transmission electron microscope (HRTEM) images of the nanoparticles were obtained with a FEI CM200 field emission TEM operating at accelerating voltage of 200 kV. Sample preparation was done by dispersing powder in methanol and ultrasounded for a few minute and then one drop pipetted onto a carbon support film on a 3 mm copper grid. Image analysis on the alumina particles was carried out on various TEM images. The processing of the image files was performed on more than 500 particles using standard image analysis software "Soft-Imaging Software GmbH CM-Prof 2.11.002".

The BET (Brunauer -Emmett -Teller) surface area measurement was made using a conventional BET multi-point N_2 physisorption apparatus (Gemini 2360, Micromeritics Instruments Corp). The N_2 adsorption was measured from a six-point isotherm in a relative pressure rang of 0.05 to 0.3 at 77.3 K. The assumption for the cross-sectional area of N_2 was taken to be 16.2(^{o}A) 2 and the density used was 3.65 g/cm^3. The sample was prepared by heating at 150 ^{o}C for 1hr while simultaneously a flow of N_2 gas across the sample tube seeps away the liberated contaminants.

The particle size distribution of the powder was measured by photon correlation spectroscopy (PCS) using a Malvern Zetasizer Nano ZS laser particle size analyzer. The instrument was equipped with a He-Ne laser source (λ=633 nm) and at scattering angle of 1730. The dispersion concentration was around 0.1 g/L. The suspension was prepared by dispersing the powder in distilled water and treated for 6mins in an ultrasonic bath to obtain a well-dispersed suspension.

The XRD pattern of the sample was collected at room temperature on a Philips X'Pert Pro diffractometer, equipped with Cu target X-ray tube with step size of 0.020 2è and time per step of 0.3s.

3. RESULTS AND DISCUSSION

3. 1. Transmission Electron Microscopy (TEM)

The TEM can yield information such as particle size, size distribution and morphology of the nanoparticles. In particle size measurement, microscopy is the only method in which the individual particles are directly observed and measured [8]. Typically, the calculated sizes are

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expressed as the diameter of a sphere that has the same projected area as the projected image of the particle. Manual or automatic techniques are used for particle size analysis. Manual technique is usually based on the use of a marking device moved along the particle to obtain a linear dimensional measure of the particle added up and divided by the number of particles to get a mean result [9]. TEM images can also be used to judge whether good dispersion has been achieved or whether agglomeration is present in the system. Electron microscopy requires elaborate sample preparation and is slow and few particles are examined. In combination with diffraction studies, microscopy becomes a very valuable aid to the characterization of nanoparticles [10].

Figure 1 illustrates HRTEM images of as-synthesized Al_2O_3 nanoparticles. The images show typical degrees of agglomeration and polydispersity obtained in a thermal plasma process. Typical nanoparticles are agglomerates of several primary particles. The agglomerates are termed as secondary particles. They formed when primary particles are held together by weak surfaces forces (soft agglomerates) such as van der Waals or capillary forces or by strong chemical bonds (hard agglomerates) [1].

The particle size data were obtained from the counting of more than 500 particles. Particle size and size distribution data can be represented in either a tabular or graphical form. Table 1 summarizes the particle size data extracted form the TEM images.

Table 1. The particle size data extracted form the TEM images.

Mean (nm)	24
Median (nm)	21.46
Mode(nm)	15.85
Standard Deviation	12.1
Kurtosis	5
Skewness	1.6
Range(nm)	89.4
Minimum(nm)	5.6
Maximum(nm)	95.1
Sum	12867.8
Count	535

Based on the particle size data given in table 1, particle size distribution was plotted. A typical way to present the particle size and its distribution is in the form of a number-frequency histogram. A histogram is a bar graph that illustrates the frequency of occurrence versus the size range [11, 3]. Figure 2 shows number frequency histograms of particle size data in linear scale. The smooth curve drawn through the histogram is a valid size-frequency curve if sufficient particles are counted and the size interval is at least ten. Hundreds of particles should be measured to present statistically reliable mean size data. For instance, it has been

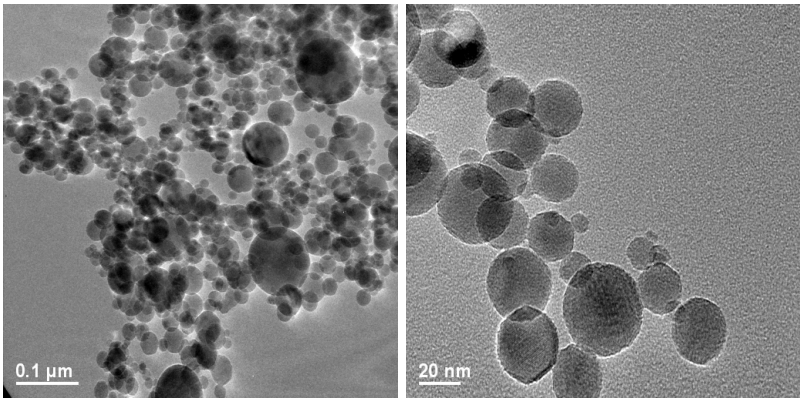

Fig. 1. High-resolution TEM (HTREM) images of plasma-synthesized alumina nanoparticles.

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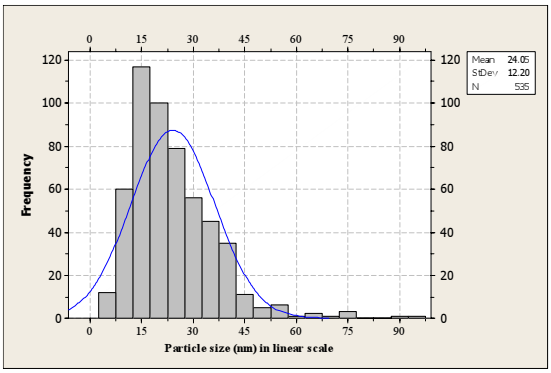

Fig. 2. Number frequency histograms showing particle size distribution of plasma-synthesized alumina nanoparticles in linear scale. The particle size data is based on the image analysis of more than 500 particles.

proposed to measure 500-1000 grains for an optimum sample size [12, 13].

As it is observed in Fig.2, the size distribution of the particles is skewed toward the larger end of the particle-size scale as the majority of real powder samples when plotted on the linear scale [14].

Despite the fact that the histogram reveals the range of the particle size, it is often insufficient for finding a mathematical formula which fits the distribution due to its shape changes with the particle number. Thus, the particle size results are also plotted as cumulative percentage frequency curves as are shown in Fig.3. These curves can be plotted with either linear or logarithmic scales. From the plots, one can estimate the median and standard deviation. Another advantage of this plotting method is that it is easier to find a better fitting mathematical formula for the distribution. To verify this, we plot the cumulative percentage curve with particle size axis in linear scale, Fig.3a. If the distribution is governed by a normal or Gaussian distribution formula, they should have a straight-line fit [8, 12]. However, the figure reveals that the distribution lies on significantly curved lines, which means that Gaussian does not adequately describe the distribution. On the other hand, Fig 3.b contains the same data with a logarithmic scale of the particle size, and the distribution is fairly straight, which implies that the data can be more accurately represented by a log-normal distribution formula. This governing formula is also verified in the figure by solid line reflecting best-fit log-normal distribution.

To characterize the particle shape, different shape factors are used. The irregularity parameter (IP) is a simple concept that is employed to calculate the sphericity of particles. This descriptor is used when particle size is measured by microscopy method. For anisotropic particles with a relatively regular morphology such as a rod or plate one can define the irregularity parameter as the ratio of longest directions (the major axes) to perpendicular to the directions (the minor axes) [6, 8].

$$IP = Major\ axis/Minor\ axis$$

The irregularity parameter of a perfect sphere is unity.

As can be seen in the Fig.1, the spherical shape

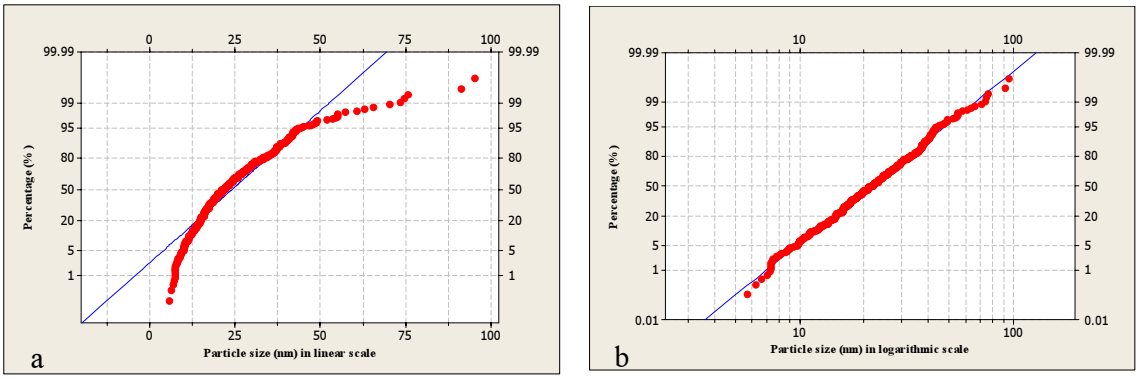

Fig. 3. Cumulative percentage frequency curves with particle size axes in (a) linear and (b) logarithmic scales. Solid line in (a) and (b) reflects Gaussian and log-normal distributions respectively.

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of the particles can appreciated from the IP equals to 1 and also the circular shape of the particle projection. Thermal plasma process has been found to produce the spherical nanoparticles as discussed in the literature [15, 16].

3. 2. X-ray Diffraction Peak Broadening Analysis

As a primary characterization tool for obtaining critical features such as crystal structure, crystallite size, and strain, x-ray diffraction patterns have been widely used in nanoparticle research. The randomly oriented crystals in nanocrystalline materials cause broadening of diffraction peaks. This has been attributed to the absence of total constructive and destructive interferences of x-rays in a finite-sized lattice. Moreover, inhomogeneous lattice strain and structural faults lead to broadening of peaks in the diffraction patterns [1]. The size calculated from x-ray diffraction peak broadening is a measure of the smallest unfaulted regions or coherently scattering domains of the material. In fact, this is the size of regions bounded by defects and grain boundaries and separated from surrounding by a small misorientation, typically one or two degrees [17].

Three methods of Williamson and Hall, Warren and Averbach and Scherrer can be used to calculate crystallite size, and strain. The simplest and most widely used method for estimating the average crystallite size is from the full width at half maximum (FWHM) of a diffraction peak using the Scherrer equation as follow:

$$d_{XRD} = \frac{K\lambda}{BCos\theta}$$

Where d is the crystallite size, λ the diffraction wavelength, B is the corrected FWHM, θ is the diffraction angle and K is a constant is close to unity. The major assumption is that the sample is free of the strain [1].

B can be obtained from observed FWHM by convoluting Gaussian profile which models the specimen broadening B_r , as follows:

$$B^2_r = B^2_0 - B_i^2$$

Where B_0 is observed broadening and B_i is instrumental broadening.

Williamson and Hall is a simplified integral breadth method for deconvoluting size and strain contributions to line broadening as a function of 2θ . They lead to a Williamson-Hall in which the y-intercept can be used to calculate crystallite size, while strain can be calculated from the

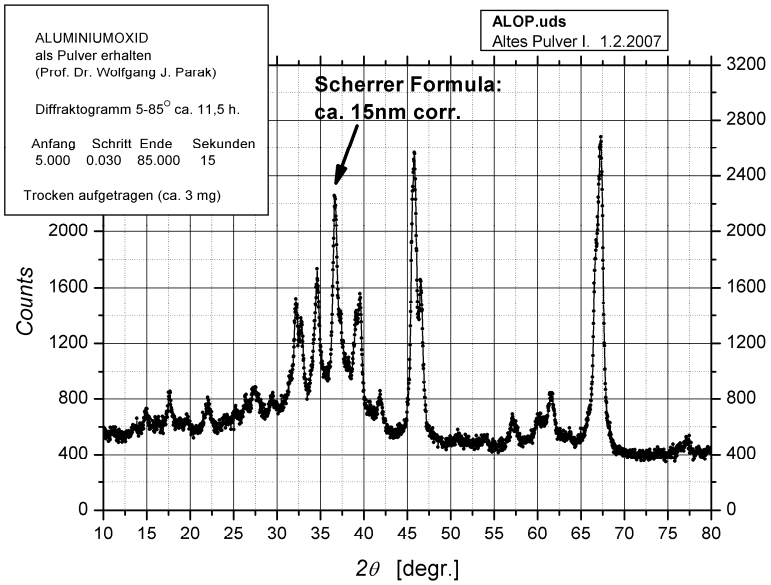

Fig. 4. The XRD pattern of alumina nanopaticles.

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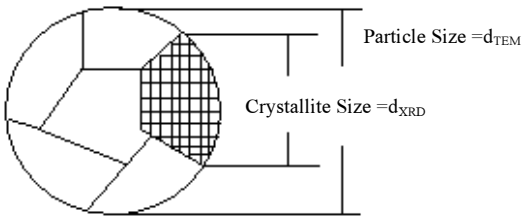

Fig. 5. Schematic showing the size that is obtained by TEM and x-ray diffraction peak broadening analysis. In the case of single-crystal nanoparticle, crystallite size and particle size are the same.

slope. Warren and Averbach's method takes not only the peak width into account but also the shape of the peak. This method is based on a Fourier deconvolution of the measured peaks and the instrument broadening to obtain the true diffraction profile. This method is capable of yielding both the crystallite size distribution and lattice microstrain [17, 18].

Fig.4 illustrates the XRD pattern of the alumina nanoparticles. Instrumental peak width was obtained with a standard silicon powder which has no size, defect and strain broadening. Using the Scherrer method and assuming the Gaussian profile for peaks model, the average crystallite sizes are obtained 15nm and 21.18nm for the peaks of 2θ =36.40 and 2θ =46.40 respectively.

As can be understood, these values are very close to the TEM value. The correlation between size obtained by XRD and TEM is that the XRD size is usually equals or smaller than that obtained by TEM [17]. When the particles are delineated by well-defined boundary or loose nanoparticles of ceramic materials as observed in Fig.1, XRD and TEM values are in good agreement. However, in bulk nanocrystalline materials produced by severe plastic deformation, the XRD result is usually smaller than TEM size. On the other hand, in nanocrystalline materials, the term grain is used interchangeably with crystallite to refer to the smallest single-phase and crystallized regions separated by grain boundaries. Each crystallite is itself a "single crystal" as such; it can contain any or all of the zero-, one-, or two-dimensional defects except for grain boundaries, interphase boundaries and surfaces. Usually, we will not consider the case of a single crystallite containing a three-dimensional defect like a pore or second-phase precipitate. Except for a single-crystal nanoaprticle, in which crystallite size and particle size are identical, the nanoparticles depending on the preparation conditions may have polycrystalline or single crystalline structure [18]. In fact/on the other hand, as the crystallite size approaches the particle size, we have single-crystal nanoparticles. The atomic planes within a crystallite can be directly imaged using high-resolution transmission electron microscopy (HRTEM).

High-resolution TEM images in Fig.2 show that the lattice planes extend up to the surface of the particle. The even diffraction contrast across the particles and lack of grain boundaries suggest virtually all particles are single crystal. This is

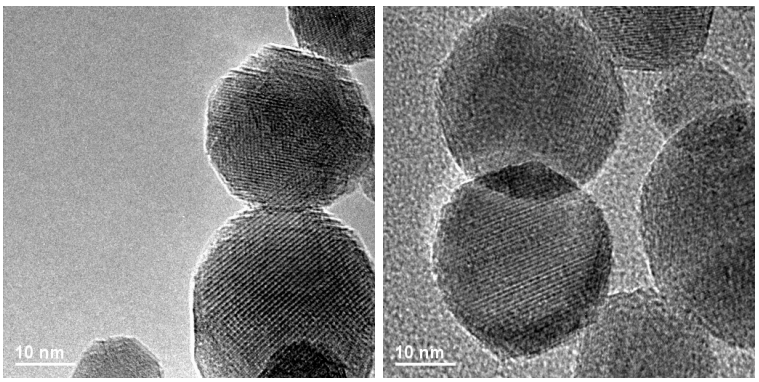

Fig. 6. High-resolution TEM (HTREM) images of the nanoparticles show the lattice planes extend up to the surface and no grain boundaries that indicate particles are single-crystal.

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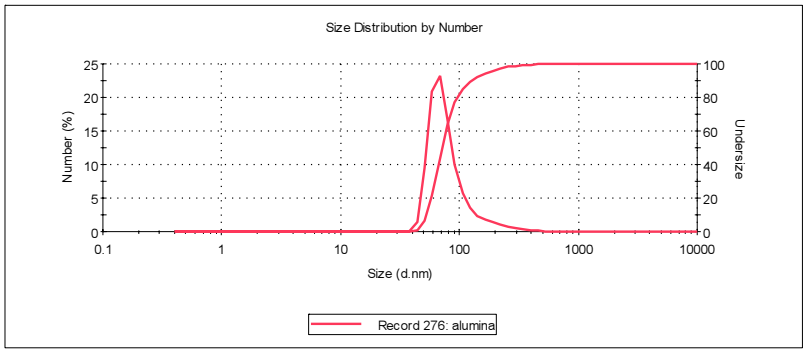

Fig. 7. Particle size distribution of the nanoparticles obtained by photon correlation spectroscopy (PCS).

confirmed by the lattice fringes at high magnification that are equal the lattice planes. The fact that they run uninterrupted across the particles again indicates particles are single-crystal. The synthesis of single-crystal nanoparticles in a thermal plasma reactor has also been reported [15].

3. 3. Surface Area Analysis (BET)

The specific surface area of the particles is the summation of the areas of the exposed surfaces of the particles per unit mass. There is an inverse relationship between particle size and surface area. Nitrogen adsorption can be used to measure the specific surface area of a powder. The method of Brunauer, Emmett, and Teller (BET) is commonly used to determine the total surface area.

If the particles are assumed to be as spherical and in a narrow size distribution, the specific surface area provides an average particle diameter in nanometer as formula below:

dBET =6000/ñs

in which S is specific surface area in m2/g and ñ is the theoretical density in g/cm3[6].

If particles do not bond too tightly, then the gas accesses most of the surface area of the powder and provides a good measure of the actual particle size independent of agglomeration. This the size of the primary particles of which the agglomerate is made up. Thus, Surface area measurement gives a value close to that obtained by electron microscopy [4, 7].

The specific surface area of the particles was obtained 60.9 m2/g. Assuming a density of 3.65g/cm^3, a mean particle size of 27 nm was calculated which agrees well with the TEM value. This indicates that the powder consists of solid spheres and gas adsorption was able to access almost the full surface area of the material that implies measurable surface was not virtually lost in interparticle contacts.

3. 4. Photon Correlation Spectroscopy (PCS)

The most common technology of the particle size distribution of nano- and submicron liquid dispersions typically is photon correlation spectroscopy (PCS) or Dynamic light scattering (DLS). PCS is a method depends on the interaction of light with particles. The light scattered by nanoparticles in suspension will fluctuate with time and can be related to the particle diameter [6, 19].

Figure 3 shows particle size distribution was obtained by PCS. Mean and median sizes obtained with PCS are 96 and 85nm respectively. These values are larger than those measured by other methods. This can be explained through dispersion of alumina powder in water and subsequent sonication. In fact, the dispersion of the alumina powder to its primary particle size does not happen completely because the attractive forces between dry particles are so great.

This is because of Brownian motion at room temperature that cause solid bridging between adjoining particles in close contact due to van der Waals attraction [7]. This is attributed to the high power (d6) dependence of the light scattering on the particle size less than 100nm according to the

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Table 2. The particle size of alumina nanoparticles obtained with TEM, XRD, PCS and BET methods.

Method	Mean diameter
	(nm)
d_{TEM}	24.1
d_{PCS}	96.2
d_{BET}	27
d_{XRD}	20

Rayleigh theory. For example, a 50nm particle will scatter one million times more light than a 5 nm particle. In order to obtain equal intensities of scattering from two particles with the size of 5 and 50nm, the presence of 1 million 5nm particles for every 50nm particle is required. Conversely, on a number basis technique such as TEM, the vast majority of particles would be 5nm. Therefore, in dynamic light scattering, the results will be sensitive to the presence of large particles (agglomerates) as they will dominate the scattering of light which is detected. On the other hand, agglomerates act as individual nonspherical particles in light scattering. The PCS method is particularly well suited to the measurement of narrow particle size distributions in the range 1–500nm, but for systems where agglomerates may be present, comparison with other methods is recommended [6].

The preceding discussion demonstrates that a number of particles properties such as shape and agglomeration are important in the particle size characterization of nanoparticles. A definition of particle size is simple for a spherical particle in which the size is uniquely defined by its diameter. Various methods of particle size analysis are used so-called equivalent spherical diameter. Equivalent spherical diameters are the diameter of spheres that have the same or equivalent length, volume and etc. as the irregular particles themselves [3, 8].

In case of this study, since the particles were spherical, there was a good agreement in TEM, BET and XRD results as is shown in Table 2. However, the difference between PCS and other results was due to the agglomerates as discussed earlier.

Moreover, it is important to be aware that each particle size characterization technique will measure a different property of a particle (volume, surface area, projected area, and etc.) and therefore will give a different value from another technique that measures an alternative dimension. This leads to many approaches to data analysis which can affect the particle size information obtained. As a result, each technique is not wrong, they all are correct; it is simply that a different property of nanoaprticle is being measured [3,7,10]. Table 3 summarizes the characteristics of methods that were employed in the present study.

5. CONCLUSION

Different techniques were used for measuring particle size of alumina nanoparticles. The

Table 3. Particle size analysis methods based on different physical principles [2, 3, 6, 8].

Method	Physical Principle	Medium	Nominal Size Range(nm)	Definition
Transmission Electron Microscopy(TEM)	Imaging/Particle Counting	Vacuum	1-6000	Diameter of a circle having the same projected area
Dynamic Light Scattering /Photon Correlation Spectroscopy	Light Scattering	Liquid	5-5000	Hydrodynamic Diameter
Gas Adsorption Surface Area Analysis (BET)	Surface Area Analysis	Gas	5-5000	Surface-volume Diameter
X-ray Peak Broadening Analysis	X-ray Diffracting	-	1-200	Coherently Scattering Domain/ Crystallite size

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particle size, size distribution and shape were determined by transmission electron microscopy (TEM). The particle size was found to be in the range of 5-95nm. Statistical analysis of TEM result indicates the particle size distribution obeys the log-normal distribution. The TEM images also reveal that particles are spherical in shape and loosely agglomerated. Comparing the XRD and TEM results shows the particles are single-crystal. The HRTEM images also justify that the particles have a single-crystal nature. In comparison, there is a good correlation between the BET, XRD and TEM measurements other than PCS that is sensitive to the presence of the agglomerates.

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REFERENCES

1. Nalwa, H.S., "Encyclopedia for Nanoscience and Nanotechnology", Vol.1, American Scientific Publishers, 2004.
2. Wang, Z. L., "Characterization of Nanophase Materials", Wiley-VCH Verlag GmbH, 2000.
3. Engineered Materials Handbook: Ceramics and Glasses: Vol.4, ASM International, 1991.
4. Staiger, M., Bowen, P., Ketterer,J. and Bohonek J., "Particle Size Distribution Measurement mand Assessment of Agglomeration of Commercial Nanosized Ceramic Particles", J. Disper. Sci. Tech., 2002, 23, 5, 619.
5. German, R. M., "A measure of the number of particles in agglomerates", Int. J. Powd. Metal., 1996, 32, 4, 365.
6. Bowen, P., "Particle Size Distribution Measurement from Millimeters to Nanometers and from Rods to Platelets" J. Disper. Sci. Tech, 2002, 23, 5, 631.
7. Rawle, A. F., "Micron sized nano-materials, Powder Technology", 2007, 174, 6.
8. Allen, T., "Particle Size Measurement, Chapman and Hall, 5th Edition", Vol.1&2, 1997.
9. Jillavenkatesa, A., Dapkunas, S. J. and Lum, Lin-Sien H., "Particle Size Characterization, NIST Recommended Practical Guide", 2001.
10. Rawle, A., "The importance of particle sizing to the coatings industry Part 1: Particle size measurement", Advances in color science and technology, 2002, 5, 1, 1.
11. ASM Handbook, Powder metal technology and application, ASM International, Vol.7, 1998.
12. Park, D., and Sinclair, R., "Grain size analysis of longitudinal thin film media", J.Appl.Phys. 2000, 87, 5687.
13. Carpenter, D. T., Rickman, J.M., and Barmak, K., "A methodology for automated quantitative microstructral analysis of transmission electron micrographs", J.Appl.Phys. 1998, 84, 5843.
14. Brittain, Harry G., "Particle Size Distribution, Part É – Representations of Particle, Shape, Size, and Distribution", Pharm.Tech. 2001, 38.
15. Carter, B., Perrey, C. R., "Insights into nanoparticle formation mechanisms", J Mater Sci, 2006, 41, 9, 2711.
16. Agarwal, Balani, K., Laha, T., Patil, S., Seal, S., "Synthesis of Nanostructured Spherical Aluminum Oxide Powders by Plasma Engineering, Metallurgical and Materials Transactions" A, 2005, 36A, 301.
17. Gubicza, J., Tichy, G., Ungára, T., "Correlation between subgrains and coherently scattering domains, Powder Diffraction", 2005, 20 (4), 366.
18. Nalwa H. S. , Handbook of nanostructrured Materials and Nanotechnology ,Vol 2: Spectroscopy and Theory", Academic Press, 2000, pp. 155-167.
19. Tinke, A. P., Govoreanu R. and Vanhoutte K., "Particle Size and Shape Characterization of Nano- and Submicron Liquid Dispersions, American Pharmaceutical Review", 2006.

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