

Micron sized nano-materials

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Abstract

The difference in “diameter” from micron to nano is 10^3 which is 10^9 (a billion) times difference in volume or mass. This implies that the properties that we have intuitive feeling for at the micron scale are considerably modified at masses a billion times smaller. Indeed it is for this reason that “nano” materials have been exploited. For example, in a 3.5 nm Au aggregate/particle (“cluster”) then about 40% of the total atoms are directly on the surface [T Shibita, H Tostmann, B Bunker, A Henglein, D Meisel, S Cheong, M Boyanov (2001), XAFS study of gold and silver-gold nanoparticles in aqueous solutions *J. Synchrotron Rad.*, 8, 545–547. [1]] introducing novel catalytic properties not present in the larger systems. As another example, gold clusters supported on a substrate will reach the melting point of solid gold only if they contain 1000 or more atoms [Michael A. Duncan and Dennis H. Rouvray, (1989), Microclusters, *Scientific American*, December 1989 issue, 110–115. [2]].

Measurement of particle size in such systems is a complex issue with each sizing technique describing different aspects of the particulate system.

We report a study of a ceramic material, barium ferrite, characterized by BET and laser diffraction where the term “nano” could be applied to the former measurements and micron to the latter technique. The reasons for the different interpretations of the result sets in the 2 cases are discussed. The ratio between the BET and diffraction results enables a measure of the agglomeration in the system to be defined. Thus “nanopowders” are collections of micron sized and larger agglomerates and aggregates and which simultaneously exhibit both nano and micron based properties.

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1. Introduction

Regis [3] quotes Eric Drexler as stating “The micron scale is volumetrically 10^9 times larger than the nanometer scale. Confusing microtechnology with molecular technology is like confusing an elephant with a ladybug”.

Data on the mass of the ladybug is difficult to come by, even though it is assumed to be spherical [4], to have a bitter taste and also to consume its weight in aphids each day at the larval stage. In contrast, adult ladybug beetles are stated as eating as many as 30–50 aphids per day. Have we a potential number–mass confusion here? Data relating to the African elephant (cow – not bull – stated mass of 3500–4500 kg) is more readily accessible. Using an estimated mass of 35 mg (Google cached search) for the ladybug, the elephant/ladybug mass ratio is estimated to be $4000/(35 \times 10^{-6})$ or around $10^8:1$. Drexler’s comment can be seen to be reasonable as the ratio of the masses of the 2 creatures does actually approach 10^9 .

Theoretical calculations supported from time to time by appropriate practical work do indicate the different properties expected for nanoscale materials. A Table from Luther [5] summarizes some of these expected or promised properties:

Properties	Examples
Catalytic	Better catalytic efficiency through higher surface-to-volume ratio
Electrical	Increased electrical conductivity in ceramics and magnetic nanocomposites, increased electrical resistance in metals
Magnetic	Increased magnetic coercivity up to a critical grain size, superparamagnetic behavior
Mechanical	Improved hardness and toughness of metals and alloys, ductility and superplasticity of ceramic
Optical	Spectral shift of optical absorption and fluorescence properties, increased quantum efficiency of semiconductor crystals
Sterical	Increased selectivity, hollow spheres for specific drug transportation and controlled release
Biological	Increased permeability through biological barriers (membranes, blood–brain barrier etc.), improved biocompatibility

It is against this background that we will describe work carried out on a material claimed to be nanosized (with supporting surface area evidence) but exhibiting other characteristics (Brownian

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motion, sedimentation rate, light scattering) typical of micron-sized materials.

2. Materials and methods

Barium ferrite ($\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$; also written as $\text{BaFe}_{12}\text{O}_{19}$) powder was obtained from a commercial supplier who uses it as a major component of low-loss ceramic magnets.

BET surface area measurements were made, by this supplier, using a conventional BET multi-point N_2 physisorption apparatus (e.g. [6,7]). The assumption for the cross-sectional area of N_2 was taken to be $16.2(\text{\AA})^2$ and the density used in the conversion of m^2/cm^3 to m^2/g was 6.31 g/cm^3 .

Powder size distributions were ascertained by means of a Malvern Mastersizer Microplus (0.05–550 μm) with measurements occurring after wetting in water and ultrasonic dispersion to stability. Optical properties used in the Mie theory deconvolution from the collected intensity-angle data to particle size distribution result were 2.59/0.1/1.33. The standard equation $\text{SSA}=6/D[3, 2]$ was the basis for the comparative data described below.

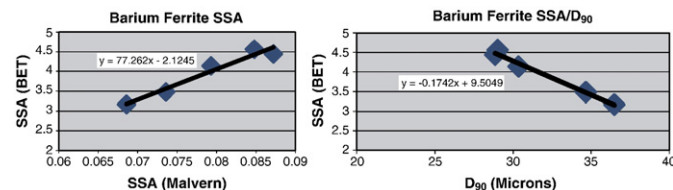
3. Results

The key laser diffraction particle size and BET parameters can be summarised in a single Excel table:

Sample ID	D_{10} μm	D_{50} μm	D_{90} μm	D [3, 2]	Malvern SSA (m^2/g) [*]	BET SSA (m^2/g)	B/M	D_{90} [*] SSA	BET Size [*] μm	BET Size [*] nm
Sample 1	8.04	18.15	36.47	13.86	0.0686	3.16	46.1	115.2	0.30	301
Sample 2	7.03	15.75	34.65	12.93	0.0736	3.48	47.3	120.6	0.27	273
Sample 3	7.07	15.8	30.34	11.98	0.0793	4.14	52.2	125.6	0.23	230
Sample 4	6.4	14.36	28.85	10.91	0.0872	4.44	50.9	128.1	0.21	214
Sample 5	6.64	14.8	29	11.22	0.0848	4.56	53.8	132.2	0.21	209
						MEAN	50.0	124.4		

^{*} Assumes density of 6.31 g/cm^3

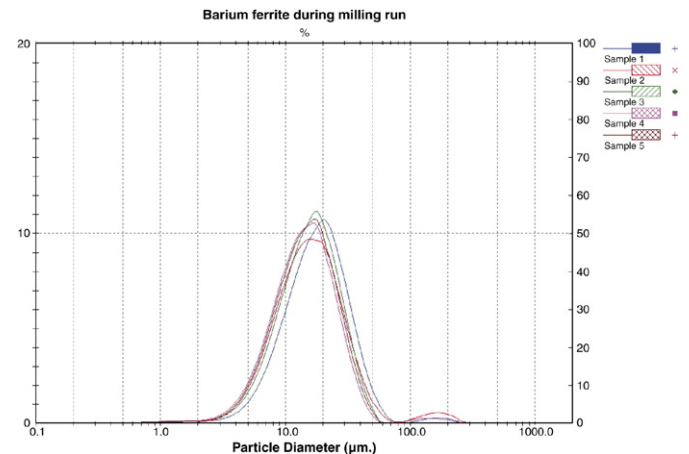
We note an approximately linear relationship between the BET and laser diffraction surface areas indicating that the more rapid laser diffraction measurement can be used as a guide to the surface area. More interesting is the correlation between the D_{90} and the measured BET surface area:



The customer was using the BET surface areas to control the barium ferrite milling process. The surface area is greatly influenced by the small material (rather than the larger in the system), so that a D_{90} correlation is normally not made or even considered. However, as only the large particles are processed within a ball mill (and hence control is possible on the single parameter of say D_{90} or D_{95} reflecting the top-end material)

then we sought to use a single laser diffraction parameter to control the mill — this could be D_{95} or the derived/calculated SSA figure obtained from the $D[3, 2]$.

The frequency plots show the removal of agglomerates in the milling process but also show the difficulties of interpretation, as the changes during the milling process are not marked:



We note too the differences between the calculated SSAs from laser diffraction and those higher surface area values obtained by N_2 BET. The ratio between the 2 figures allows an apparent agglomeration figure ($=B/M$ in the table) to be calculated in a similar manner to those definitions proposed by Adair [8] and German [9]. The ratio in this case is (rather spookily given our obsession with integral numbers) around 50.0.

Although the back-calculated size by BET (200–300 nm) does not fall strictly into the $<100 \text{ nm}$ definition of ‘nano’ [10,11] — perhaps sub-micron is better [12] — it could easily be used to justify a definition of “nanopowder” for the material. The median diffraction result for the smallest measured material of just under $15 \mu\text{m}$ does not appear at first to be comparable, or even correct to the uneducated observer.

4. Discussion

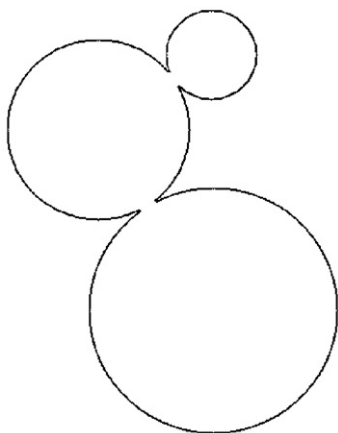
All dry powders consist of (“soft”) agglomerates and (“hard”) aggregates [13,14]:

Agglomerate adhesion mechanisms (after Halloran)	
Soft agglomerates	Hard agglomerates (aggregates)
van Der Waals forces	Solid bridges caused by:
Adsorbed moisture	1. Sintering
Capillary-condensed liquids	2. Phase transformation
Viscous binders	3. Solid State reactions
	Cementitious bond
	Strong glassy binders

In wet systems, the word colloid, which we associate with small-suspended matter, derives from the Greek for glue, $\kappa\omicron\lambda\lambda\alpha$ or $\kappa\delta\lambda\lambda\eta$. Brownian motion at room temperature in small (“nano”) primary sized particles typically smaller than 100 nm is sufficient to cause solid bridging between adjoining particles in close contact due to van der Waals attraction. These

hard aggregates are virtually impossible to “disperse” without dissolving the solid bridges in what is termed ‘stress corrosion milling’.

We can explain both the ‘nano’ and “micro” results by imagining a bridged system as below:



If these are spherical particles of 1, 2 and 3 units respectively, bonded together by 5% of the available surface area, then our calculated sizes will be:

Technique	Calculated average or mean	Type of diameter	Comments
Image analysis/microscopy	2.00	$D[1, 0]$	Number average erosion–dilation measure of size
BET	2.22	$D[3, 2]$	Back extrapolation from surface area measurement Assumes 95% of total surface (14 units) available for gas absorption $(6/[(0.95 \times 14)/36])$
Project area (single particle counter)	3.23	Equivalent projected area	Assumes 5% reduction in area due to solid bridging $(0.95 \times [14\pi/4])^{(0.5)}$
Light scattering	3.30	$36^{(1/3)}$	Volume average, based on volume equivalent of fused particles (Total volume=36 cubic units). Single particle calculation (not $D[4, 3]$)
Brownian Motion	?	Hydrodynamic/Stokes'	Particle shape will affect movement through fluid in a difficult to predict manner
Sedimentation	?	Hydrodynamic/Stokes'	See Brownian Motion. Particle unlikely to settle in a straight line

We see here the propensity for visualization techniques such as SEM to give a number mean biased towards the smallest particles in the system. Likewise, the volume-based technique (equivalent to the \$ distribution) will favour the larger particles in the system. Surface area measurement by BET when back extrapolated may give a value quite close to that obtained by (electron) microscopy. However, that particulate system will exhibit bulk properties (flowability, rheology, Brownian

motion/diffusion, screen passage) that differ markedly from the fundamental particle size.

In the case of the barium ferrite experiments noted above we have a (considerably) higher surface area – and therefore much smaller calculated particle size – based on BET physisorption than that calculated by laser diffraction. However, there is a good correlation and fixed constant of proportionality between the 2 independent measurement types.

A recent ANSI report [15] identifies an area within the metrology of nanotechnology as being “Most important” — Group 3 Particle Size and Particle Shape. We note that the terms “size” and “shape” in particle size analysis are related to the type of measurement undertaken and thus are easily misinterpreted by the novice. We thus welcome standardization in this area.

In conclusion, we should take great care in describing particulate systems in terms of “nano” or “micro” when, in fact, it is the end properties of the system that we require. Simple characterization numbers can lead to confusion especially when number, surface or volume-based techniques are compared. It may be that it is preferable to ask the questions: “Does our material possess the desired properties?” and “Is our material ‘fit for purpose’?” rather than “What is the size of the material?” Confusion of units is easily seen when the length of a ladybug is stated to be 5 mm ($= 5 \times 10^{-3}$ m) or alternatively 3100 nanomiles or ~25,000 nanofurlongs (8 furlongs=1 mile=1760 yards=5280 feet ~1609 m).

References

- [1] T. Shibita, H. Tostmann, B. Bunker, A. Henglein, D. Meisel, S. Cheong, M. Boyanov, XAFS study of gold and silver–gold nanoparticles in aqueous solutions, *Journal of Synchrotron Radiation* 8 (2001) 545–547.
- [2] Michael A. Duncan, Dennis H. Rouvray, *Microclusters*, Scientific American, December 1989, pp. 110–115, issue.
- [3] Ed Regis, *Nano: The Emerging Science of Nanotechnology*, 1st Edition, Little, Brown and Company, ISBN: 0-316-73858-1, 1995, pp. 207–208.
- [4] P.W. de Jong, S.W.S. Gussekloo, P.M. Brakefield, Differences in thermal balance, body temperature and activity between non-melanic and melanic two-spot ladybird beetles (*Adalia bipunctata*) under controlled conditions, *The Journal of Experimental Biology* 199 (1996) 2655–2666.
- [5] Wolfgang Luther (Editor), (2004), *Industrial applications of nanomaterials — chances and risks*. Technology Analysis Project funded by the European Community Published by Future technologies Division, VDI Technologiezentrum GmbH, Graf-Recke-Str. 84, 40239, Dusseldorf, Germany. August 2004 ISSN 1436–5928.
- [6] J.R. Anderson, *Structure of Metallic Catalysts*, Academic Press, 1975.
- [7] S.J. Gregg, K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, Inc., 1982
- [8] J.H. Adair, A.J. Roese, G.L. McCoy, Particle size analysis of ceramic powders. Processing for improved productivity, in: K.M. Nair (Ed.), *Adv. Ceramics*, vol. 11, The American Ceramic Society, 1984.
- [9] R.M. German, A measure of the number of particles in agglomerates, *International Journal of Powder Metallurgy* 32 (4) (October 1996) 365–373 (issue).
- [10] M.C. Roco, S. Williams, A.P. Alivisatos, (1999), *Nanotechnology Research Directions: IWGN Workshop report*; WTEC, Loyola College, Maryland. From: <http://www.wtec.org/loyola/nano/IWGN.Research.Directions/>.
- [11] M.C. Roco, From vision to implementation of the U.S. National Nanotechnology Initiative, *Journal of Nanoparticle Research* 3 (1) (February 2001) 5–11.
- [12] J.F. Bertone, et al., Hydrothermal synthesis of quartz nanocrystals, *Nano Letters* 3 (5) (2003) 655–659.

- [13] J.H. Adair, E. Suvaci, J. Sindel, Surface and Colloid Chemistry Encyclopedia of Materials: Science and Technology, Elsevier Science Ltd, ISBN: 0-08-0431526, 2001, pp. 8996–9006.
- [14] J.W. Halloran, (1984), Chapter 32 in Agglomerates and agglomeration in ceramic processing, pp. 404–417 in Ultrastructure Processing of Ceramics, Glasses and Composites Edited by Larry L Hench, Donald R Ulrich Wiley-Interscience, Proceedings of the International Conference held Feb. 13–17th 1983 in Gainesville, Florida ISBN: 0-471-89669-1.
- [15] ANSI-NSP Report (2004) NSP SC 027-2004 ANSI-NSP Priority Recommendations related to nanotechnology. Standardization needs. (November 15, 2004).