1706
doi:10.1017/S1431927618009017
Microsc. Microanal. 24 (Suppl 1), 2018

Size and Shape Distribution of Bipyramidal TiO_2 Nanoparticles by Transmission Electron Microscopy – an Inter-Laboratory Comparison

Vasile-Dan Hodoroaba[1], Kazuhiro Yamamoto[2] and Eric A. Grulke[3]

[1.] Federal Institute for Materials Research and Testing (BAM), Berlin, Germany.
[2.] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.
[3.] University of Kentucky, Chemical & Materials Engineering, Lexington, KY, USA.

Accurate measurement of size and size distribution of nanoparticles (NPs) is an analytical task which becomes challenging for any measurement technique once the nanoparticle shape is non-spherical. The results obtained with different sizing techniques for a set of nanoparticulate materials of high industrial relevance, having more complex particle shapes and broad size distributions can deviate with even more than a factor of two – as a recent review shows [1]. High-resolution imaging methods, above all, electron microscopy (TEM and SEM), are able to access shape of individual NPs at best, however, extraction of true, 3D shape (and size) for non-spherical NPs is also associated with errors by conventional 2D electron microscopy using projection images. Significant efforts for accurate measurement of NP size and shape with TEM and SEM as robust, standard procedures are carried out within the ISO technical committee TC 229 'Nanotechnologies'. International study groups have been organizing inter-laboratory comparisons on well-selected NP systems according to the market needs. One case study is constituted by a commercial aggregated titania powder for which size and shape distribution of primary crystallite with irregular shape must be measured accurately [2]. To be noticed is e. g. the fact that the measurement procedure allows only manual selection of the particles clearly distinguishable for analysis as well as manual definition of the contour of the imaged NPs.

Recently, in completion to the case study above, a new one on titania NPs (pure anatase, grown by hydrothermal synthesis [3,4]) of well-defined non-spherical shape, i.e. bipyramidal, has been started under similar framework conditions as for the irregular shaped titania. Figure 1 shows a representative TEM micrograph with particles tracked manually according to the measurement protocol. Overlapped particles were allowed to be considered, as long as they are clearly distinguishable. One decisive NP selection criterion was to consider only those NPs with a roundness value below 0.7. This value is the result of testing various scenarios beyond the basic assumption that NPs laying on the support foil clearly deviates from perfect circles (R=1). 15 laboratories from 7 countries have reported data after measurement of NPs on TEM grids as prepared and distributed by BAM. 3 laboratories have used STEM-in-SEM mode, one lab has used a miniTEM instrument. The overall evaluation of the size descriptors (area, Feret, minFeret, perimeter) and shape descriptors (aspect ratio, roundness, compactness, extent) by analysis of variance is just to be finished. In a first step, results of 5 laboratories have been evaluated. The corresponding cumulative distribution functions of the determined aspect ratio are plotted in Figure 2. Rather evident from Figure 2, but particularly according to pairwise ANOVA *p*-values for the aspect ratio datasets, results of L3, L7 and L12 may be considered as similar, while datasets L8 and 13 are different. In particular, L8 and L13 aspect ratio values stretch above 0.7 up to 0.8. Assuming normal distributions for fitting, the resulting grand of the scale and width parameters are associated by a measurement uncertainty of the scale parameter of ~7% and a measurement uncertainty of the width parameters of ~28%.

An additional exercise has been organized to quantify only the operator bias at the manual delimitation of the NPs. For this purpose, a set of 100 NPs was pre-defined by BAM in 3 TEM images distributed to 6 laboratories. The result is an excellent agreement between all 6 laboratories, i.e. an insignificant uncertainty caused by manual NP delimitation, see Table 2. One primary conclusion is that, of all descriptors, the best agreement belongs to 'aspect ratio'.

References:

[1] F Babick *et al*, J Nanopart Res **18**:158 (2016), 40 pp.
[2] EA Grulke *et al*, Adv Powder Technol **28** (2017), p. 1647.
[3] V Lavric *et al*, Cryst Growth Des **17** (2017), p. 5640.
[4] E Ortel *et al*, Microsc Microanal **21** (Suppl 3) (2015), p. 2401.
[5] The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n°604577. Many thanks are due to Prof. V Maurino and F Pellegrino (University of Torino) for providing the sample material. All participants in the inter-laboratory comparison are especially acknowledged.

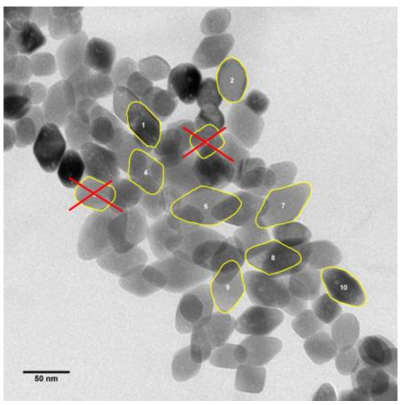

Figure 1. Representative TEM micrograph with NPs tracked manually.

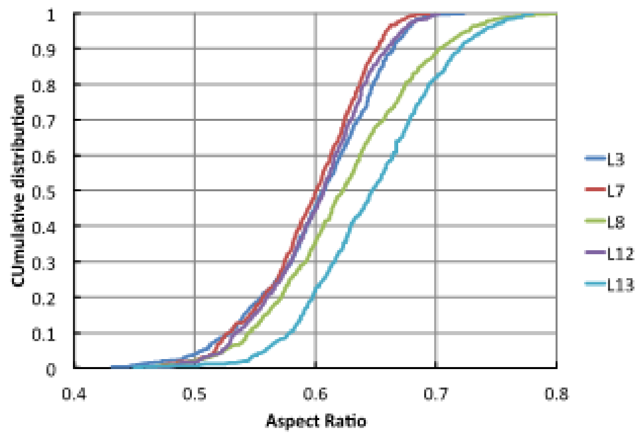

Figure 2. Cumulative distribution functions of the NP aspect ratio as obtained by 5 laboratories.

Table 1. Aspect ratio datasets with grand means of scale and width parameters.

Laboratory	**scale**	**width**
L3	0.6052	0.0530
L7	0.5988	0.0462
L8	0.6227	0.0619
L12	0.6039	0.0473
L13	0.6473	0.0579
Grand mean	0.6156	0.0533
Grand stdev	0.0199	0.0067
C_v	3.23%	12.65%
U_{ILC}	**7.08%**	**27.72%**

Table 2. ANOVA *p*-values of size and shape descriptors.

Descriptor	*p*-values	Rank order
Size		
Area	0.802	4
Feret	0.316	7
minFeret	0.165	8
Perimeter	0.621	5
ECD	0.560	6
EPD	0.165	8
Elongational shape		
Aspect ratio	0.969	1
Roundness	0.826	3
Compactness	0.830	2
Extent	0.002	9
Circularity	<0.001	10

https://doi.org/10.1017/S1431927618009017 Published online by Cambridge University Press