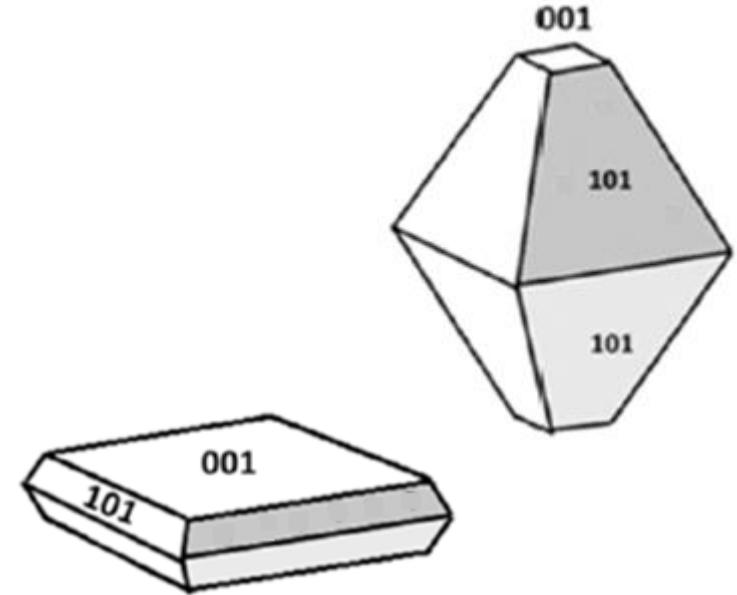


Atomic force microscopy metrology of non-spherical nanoparticles



Valter Maurino (1), Francesco Pellegrino (1), Gian Bartolo Picotto (2), Luigi Ribotta (2,3)

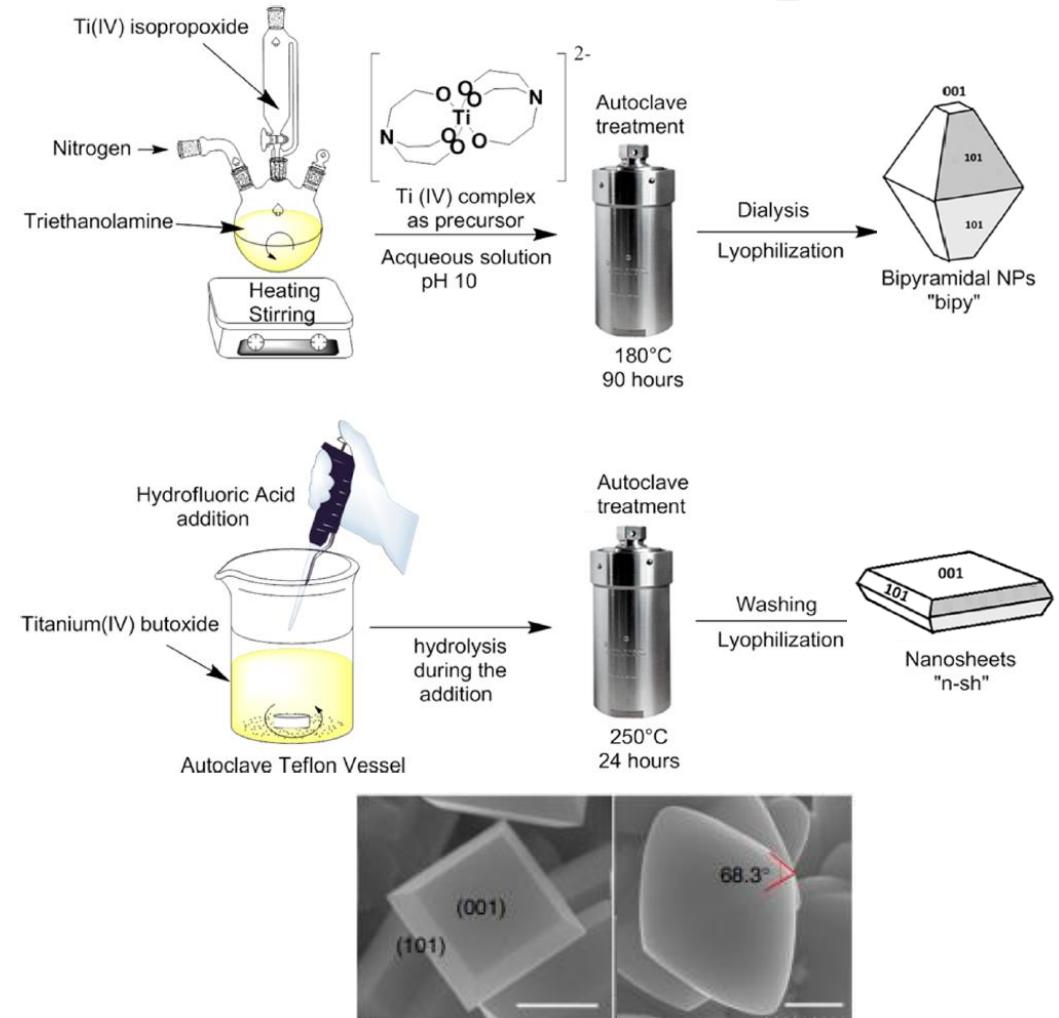
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(2) Istituto Nazionale di Ricerca Metrologica (INRiM), Strada delle Cacce 91, 10135, Torino, Italia

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Objectives

- Since size and shape of structures play a crucial role at the nanoscale, traceable 3D measurements of nanoparticles (NPs) are today an issue;
- Anatase TiO_2 non-spherical engineered NPs (e.g., bipyramids and nanosheets) are studied with metrological AFM (mAFM) as candidate reference materials for dimensional metrology;
- Non-spherical NPs present a challenge about AFM measurements, as their geometries highlight the limits connected to the finite shape and size of the tip.

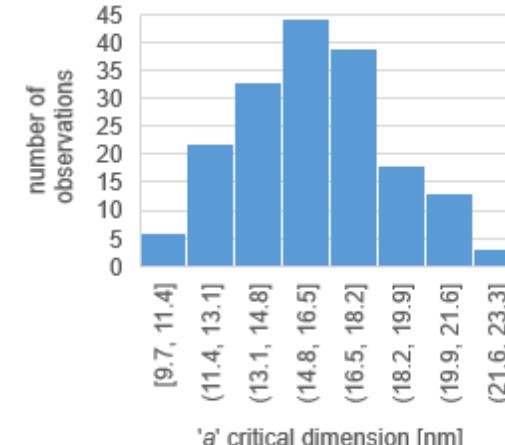
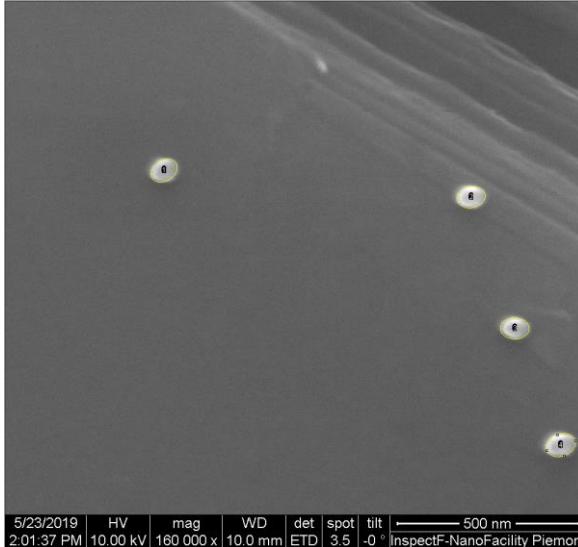
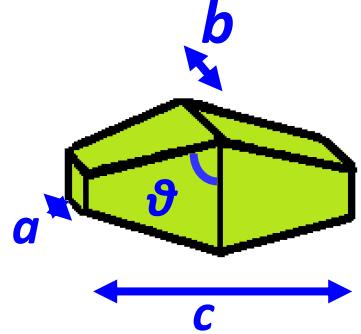


[1] L. Mino, F. Pellegrino, S. Rades, J. Radnik, V.-D. Hodoroaba, G. Spoto, V. Maurino, G. Martra, Beyond Shape Engineering of TiO_2 Nanoparticles: Post-Synthesis Treatment Dependence of Surface Hydration, Hydroxylation, Lewis Acidity and Photocatalytic Activity of TiO_2 Anatase Nanoparticles with Dominant {001} or {101} Facets, *ACS Applied Nano Materials*, 2018, 1 (9), pp 5355–5365

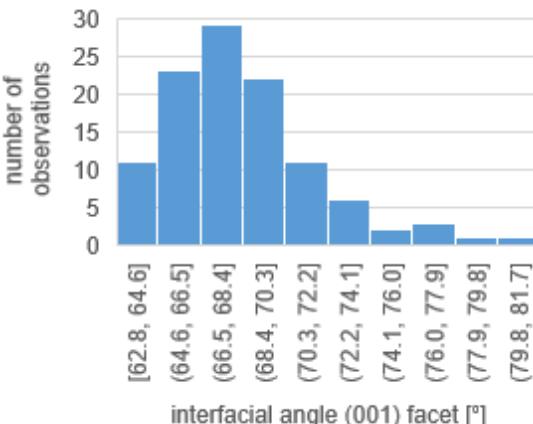
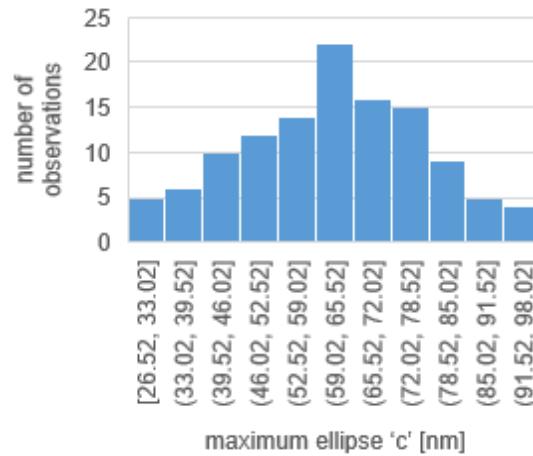
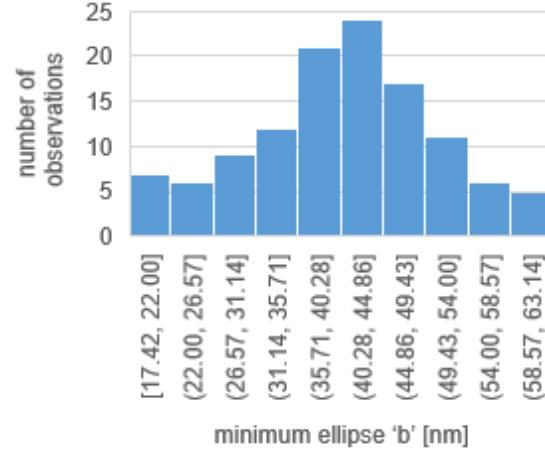
[2] S. Yang, B. X. Yang, L. Wu, Y. H. Li, P. Liu, H. Zhao, Y. Y. Yu, X. Q. Gong, H. G. Yang, Titania single crystals with a curved surface, *Nature Communications*, 5:5355, 2014

TiO₂ bipyramids

CRITICAL DIMENSION (CD) MEASUREMENTS BY SEM IMAGES



$$a = (15.9 \pm 2.7) \text{ nm}$$



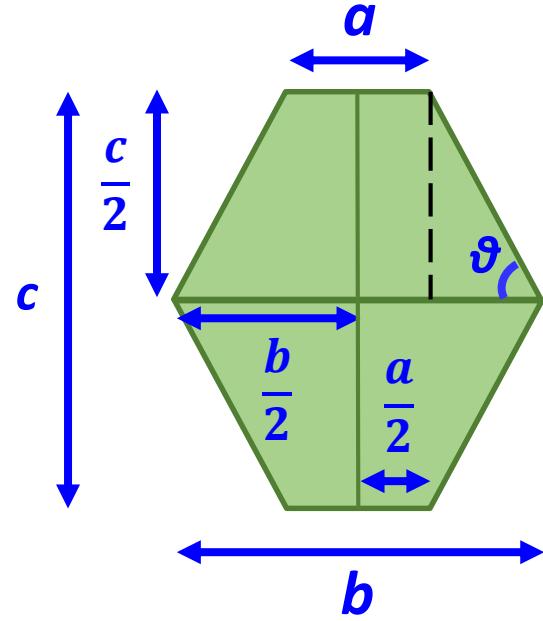
$$\vartheta = (68.3 \pm 3.5)^\circ$$

(mean value \pm standard deviation)

$$b = (39.9 \pm 11.0) \text{ nm}$$

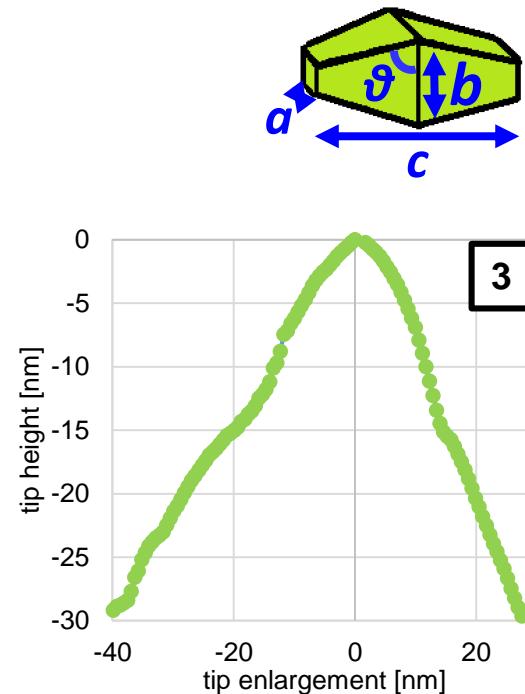
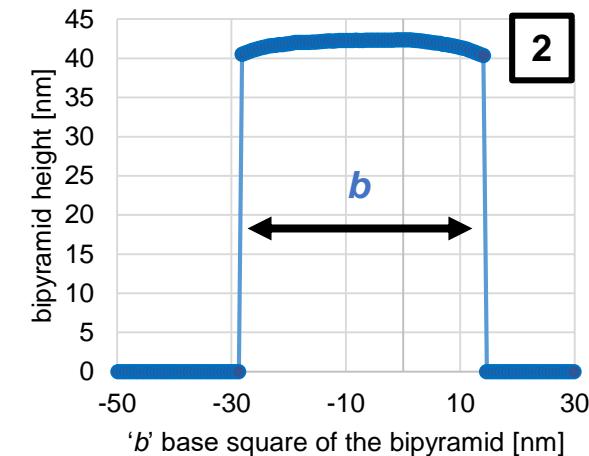
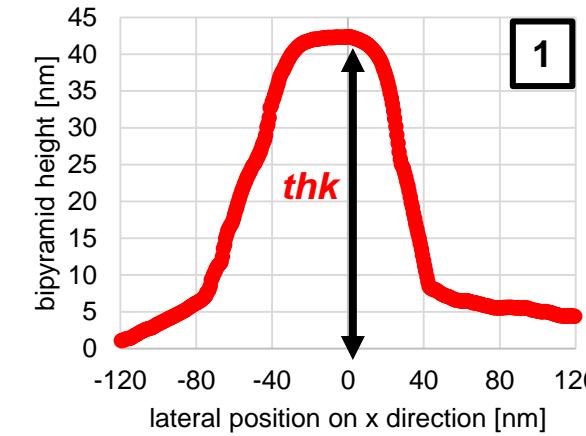
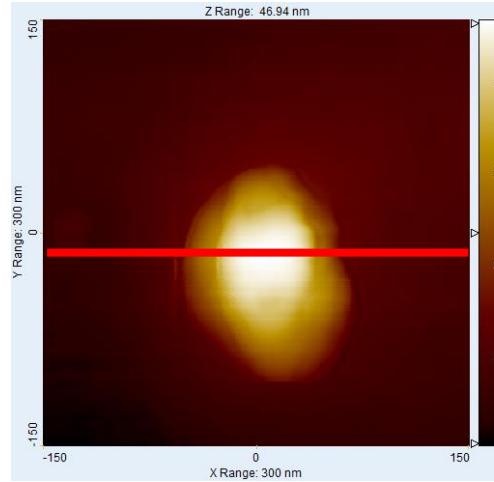
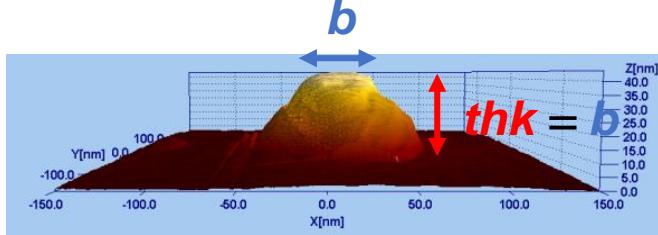
$$c = (61.2 \pm 16.8) \text{ nm}$$

number of images: 16
counted particles: 120



TiO₂ bipyramids

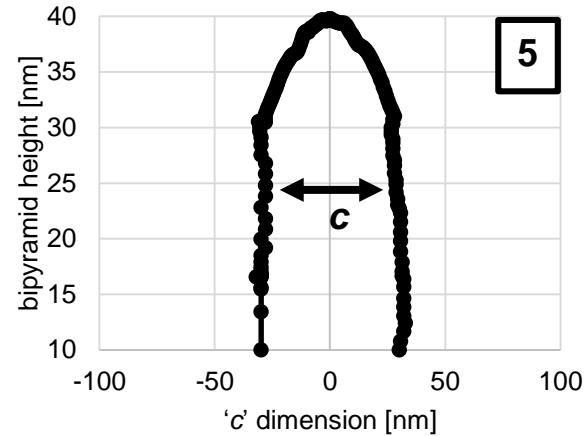
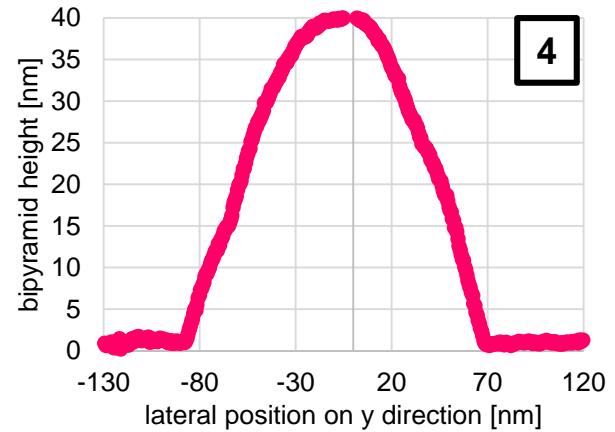
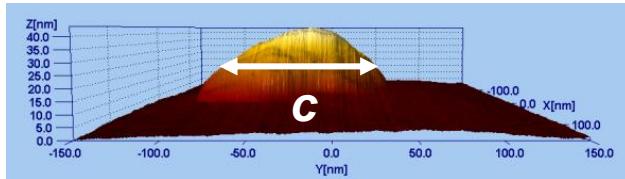
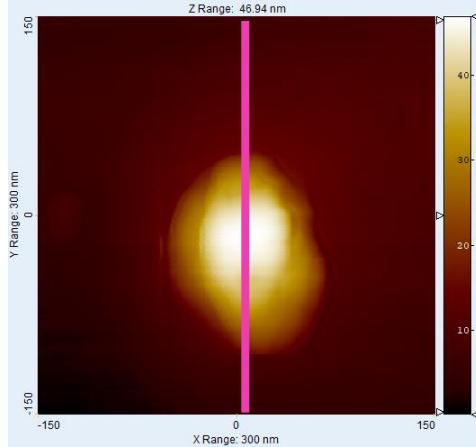
GEOMETRICAL MODEL FOR PROFILE RECONSTRUCTION BY mAFM IMAGES



- 1 Mean cross-section top profile at the bipyramid base; step-height **thk**.
- 2 Square base of the bipyramid as obtained from profile 1 **b = thk**.
- 3 Tip enlargement as estimated by assuming a square base of the bipyramid **b**.

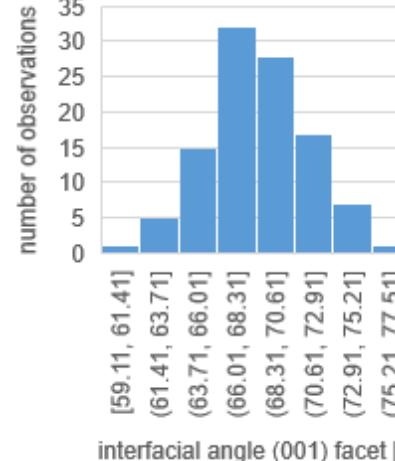
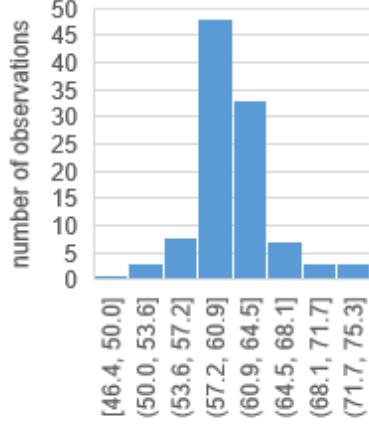
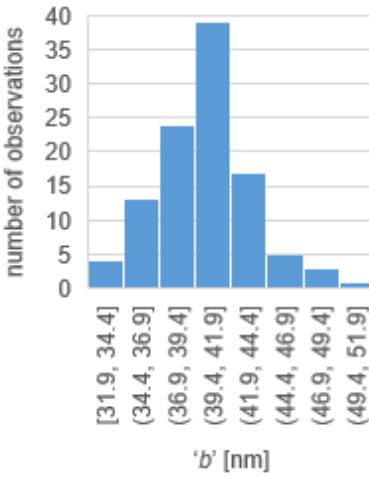
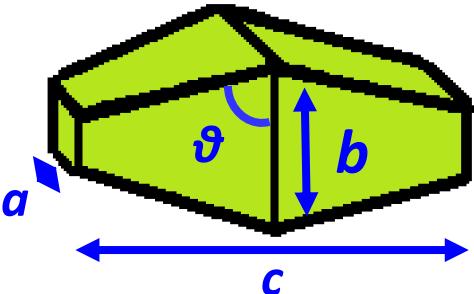
TiO₂ bipyramids

GEOMETRICAL MODEL FOR PROFILE RECONSTRUCTION BY mAFM IMAGES



- 4 Mean top profile along the main axis of the bipyramid.
- 5 NP 'c' size as obtained by subtracting the tip enlargement profile (profile 3) the to the top profile (4). Tip enlargement is assumed to be isotropic along the x and y axes.

CD MEASUREMENTS BY mAFM IMAGES



$$b = (40.1 \pm 3.4) \text{ nm}$$

$$c = (60.8 \pm 4.3) \text{ nm}$$

(mean value \pm standard deviation)

number of images: 106

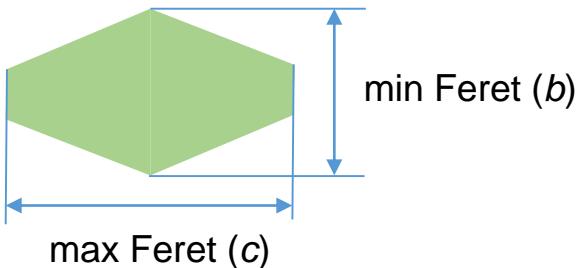
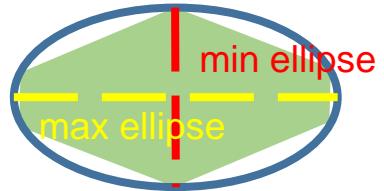
counted particles: 106

uncertainty budget of 'b'

quantity	type	probability distribution	uncertainty contribution $u(x_i)$ [nm]	sensitivity coefficient $c_i = \frac{\partial f}{\partial x_i}$	uncertainty $u_i(b)$ [nm]	degrees of freedom v_i
repeatability	A	N	0.30	1	0.30	106
z-stage calibration	B	N	0.40	1	0.40	100
z-stage resolution	B	R	0.10	0.58	0.10	100
profile noise	A	N	0.50	1	0.50	50
reference plane	A	R	1.00	0.58	0.60	50
sample flattening	A	R	0.50	0.58	0.30	50
geometrical model	A	R	0.01	0.58	0.01	50
tip geometry	B	R	0.30	0.58	0.20	10
combined standard uncertainty					1.1	280

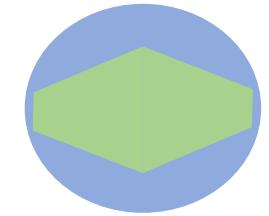
TiO₂ bipyramids

SIZE AND SHAPE DESCRIPTORS

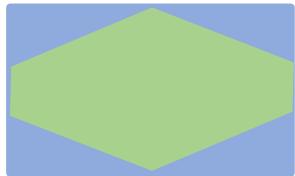


elongation $E = \frac{\text{max Feret}}{\text{min Feret}}$

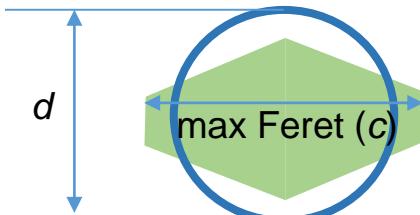
aspect ratio $AR = \frac{\text{min Feret}}{\text{max Feret}}$



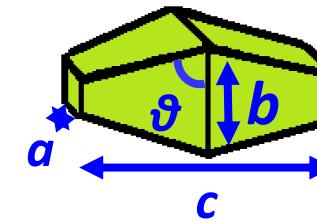
roundness $R = \frac{A}{\pi \left(\frac{\text{max Feret}}{2} \right)^2}$



extent, bulkiness $B = \frac{A}{\text{max Feret} \cdot \text{min Feret}}$



compactness $cmp = \frac{\sqrt{\frac{4 \cdot A}{\pi}}}{\text{max Feret}} = \frac{d}{\text{max Feret}}$

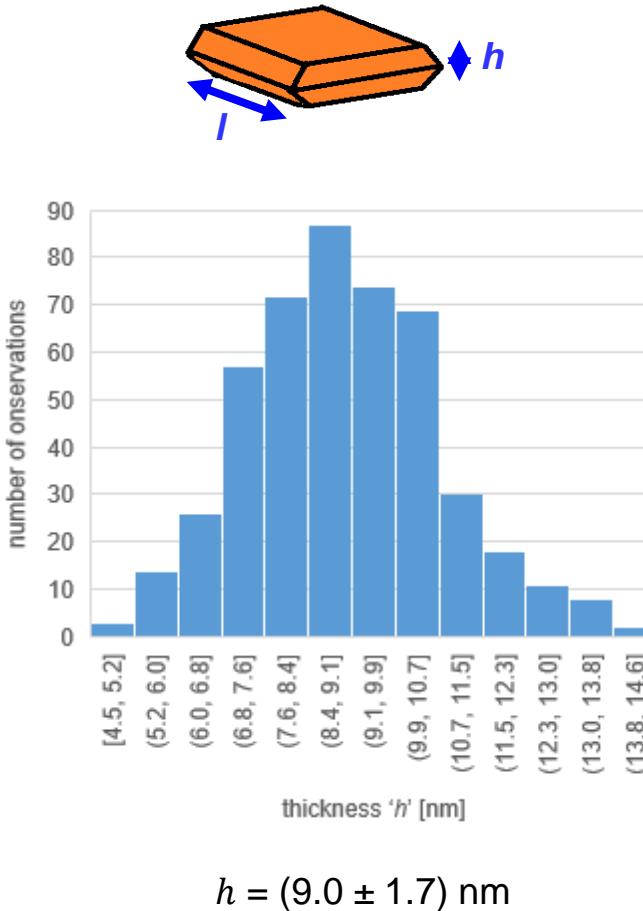


Descriptor	SEM measurements [nm]	AFM measurements [nm]	$\Delta [\%]$
max ellipse	61.2 ± 16.8	-	-
min ellipse	39.9 ± 11.0	-	-
max Feret	61.6 ± 17.0	60.8 ± 4.3	1.3
min Feret	39.9 ± 11.0	40.1 ± 3.4	0.4
aspect ratio	0.6 ± 0.1	0.7 ± 0.1	0.8
elongation	1.5 ± 0.1	1.5 ± 0.2	1.4
roundness	0.6 ± 0.1	0.7 ± 0.1	2.2
bulkiness	0.8 ± 0.1	0.8 ± 0.1	0.7
compactness	0.8 ± 0.1	0.8 ± 0.1	1.3

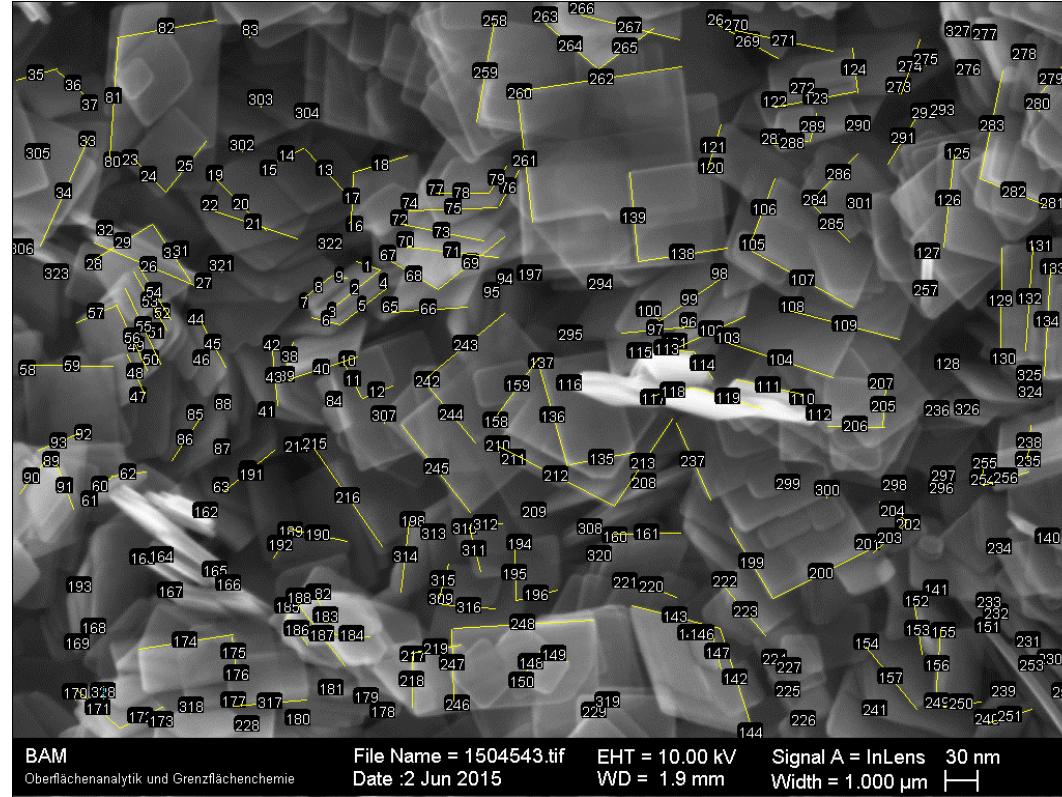
(mean value \pm standard deviation)

TiO₂ nanosheets

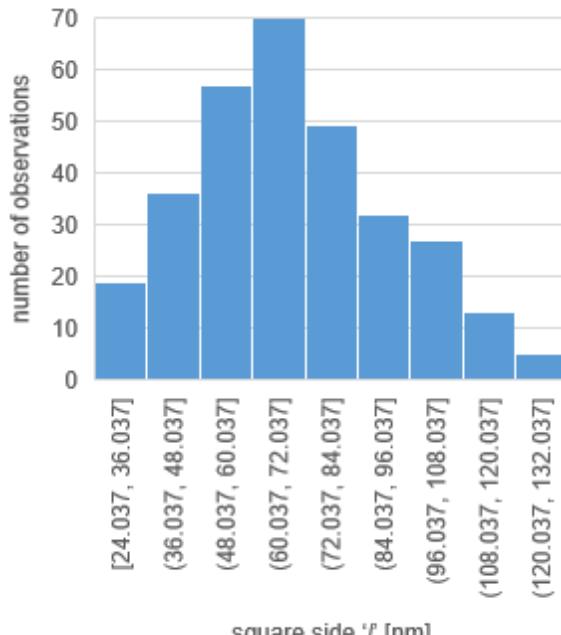
CD MEASUREMENTS BY SEM IMAGES



number of images: 4 images
counted nanosheets > 300



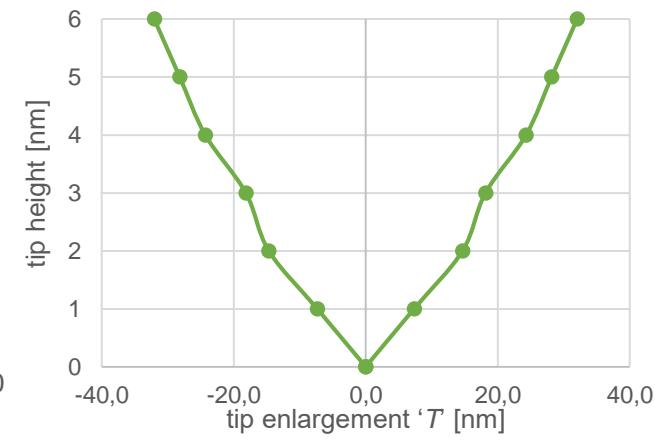
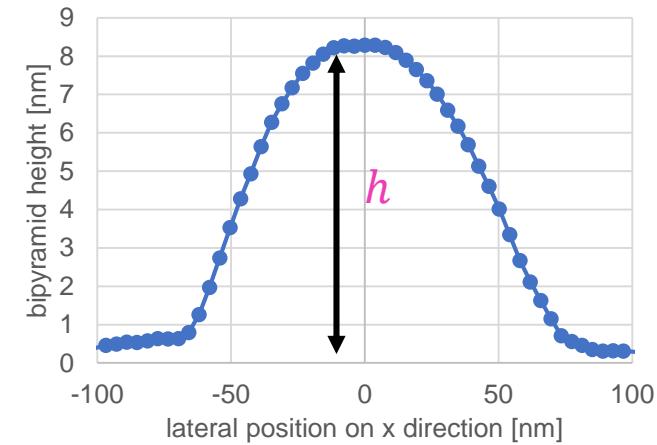
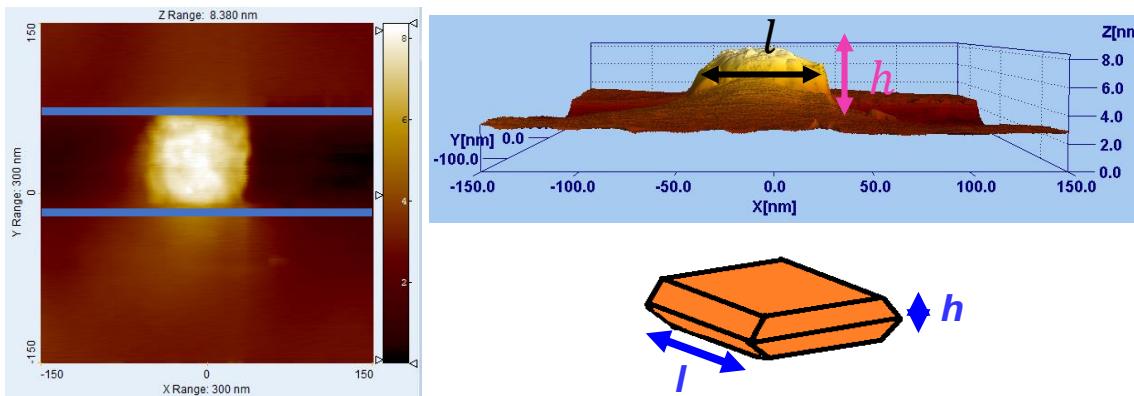
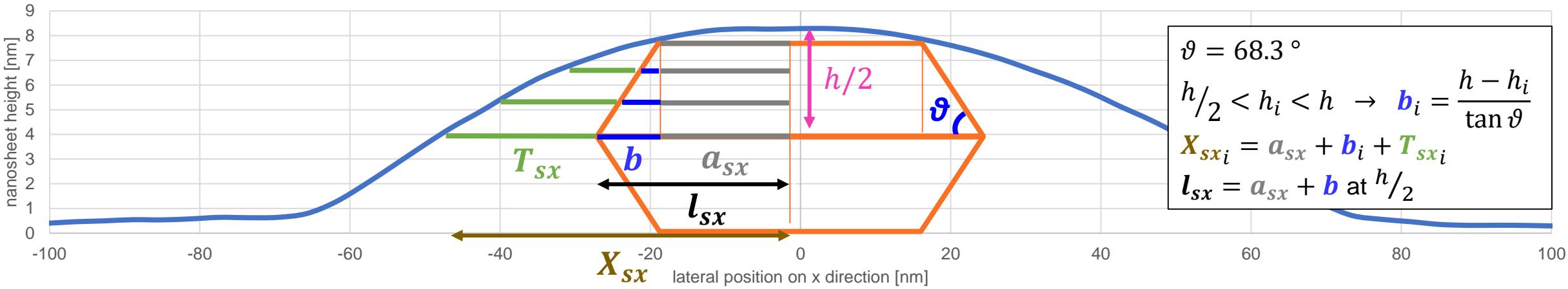
SEM image of TiO₂ nanosheets (courtesy of BAM).



(mean value \pm standard deviation)

TiO₂ nanosheets

PROFILE RECONSTRUCTION BY mAFM IMAGES



Conclusions

- A geometrical method for CDs reconstruction of complex geometry nanoparticles in AFM-based images has been tested and implemented by an own soft-tool in MATLAB;
- Tip shape enlargement has been corrected by a geometrical profile-based approach.

- Measured CDs (a , b , c) of the bipyramids by mAFM and SEM measurements show differences within 3 %.
- Preliminary results of thickness and lateral sizes of nanosheet by mAFM and SEM measurements look also well in agreement.

Thank you for your attention!