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Traceable Dimensional Metrology of Nanoparticles and Nanostructures

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ABSTRACT

Nanometrology covers a wide range of techniques for the characterization and measurement of materials at the nanoscale. In particular, metrological Atomic Force Microscopes (mAFMs) are the workhorse of the dimensional nanometrology, since they use interferometers to carry out traceable measurements of the tip–sample relative position.

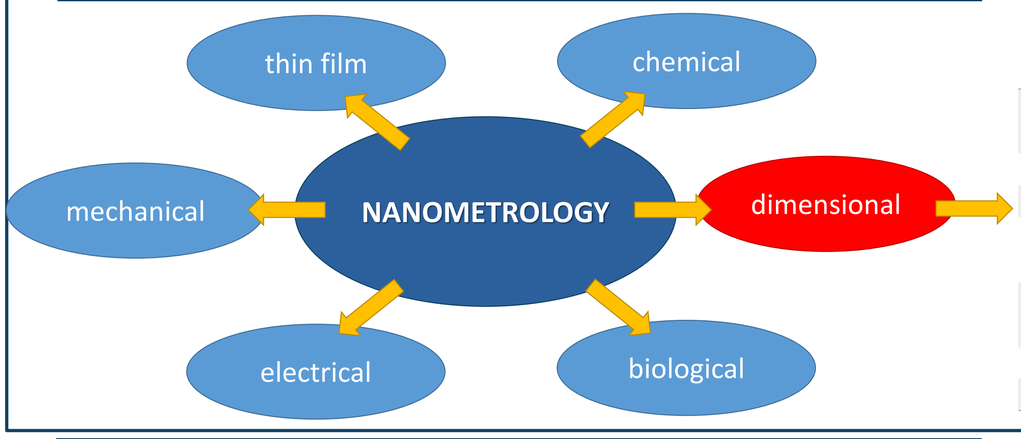
In this study, INRiM mAFM is used to study quantitatively nanoparticles (NPs) and nanostructures of different shapes.

While AFM height measurements can achieve sub-nanometer resolution and accuracy, lateral resolution is influenced by several factors, the most impacting is the tip shape. Bio-based nanostructures (Tobacco Mosaic Virus) are used as calibrator for reconstructing the dilation caused by the tip in lateral measurements, since TMV cross-sectional diameter has a stable value [1].

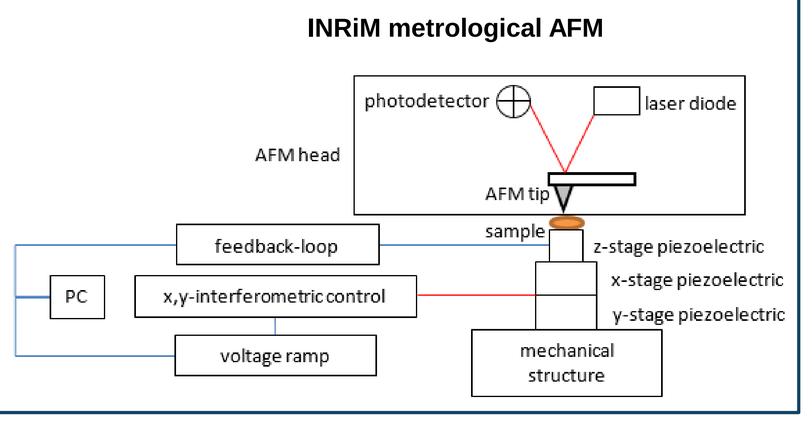
Nowadays, quasi-spherical NPs are measured sufficiently accurately by AFM, through the determination of the mean diameter as the top-height of the cross-section profile. Since industrial nanomaterials have shapes much more complex than the spherical one, traceable measurements of non-spherical shapes and sizes require the development of new measurement methods. AFM measurement of complex shape NPs represents a challenge, because their particular geometries emphasize the limitations associated with finite tip size. Through new geometrical approaches which consider the nominal crystal structure and the conditions in which the particles have been synthesized, we reconstructed robustly and accurately critical sizes and morphological parameters of TiO_2 anatase bipyramids and nanosheets NPs. These complex shape NPs can be applied as candidate reference materials in dimensional nanometrology, because of their critical sizes which are stable and have a monomodal distribution [2].

Each measurand reported in this study is determined quantitatively along with its uncertainty, with a relative combined standard uncertainty of the mean less than 10%.

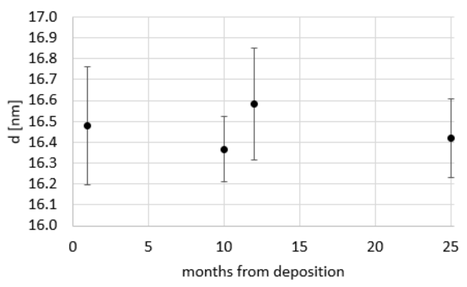
INTRODUCTION

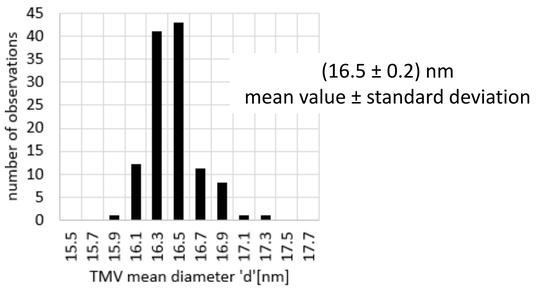


Technique	Measurand	Resolution/ Detection limits
AFM	thickness lateral size	0.1 nm (Z) 1 nm (X-Y)
SEM	mean area-equivalent diameter	1 nm
TEM	mean area-equivalent diameter	0.1 nm
DLS	scattered light intensity-weighted mean hydrodynamic diameter	3 nm
CLS	intensity-based Stokes particle diameter	20 nm
DMA	electrical mobility mean diameter	1 nm
SAXS	volume-weighted mean diameter	1 nm

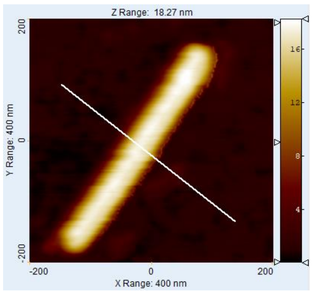


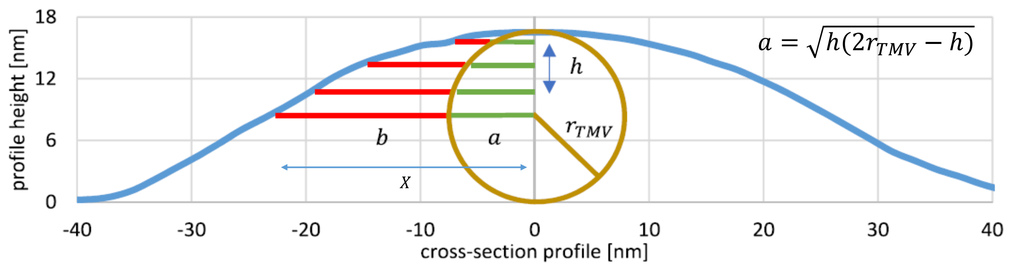
BIO-BASED NANOSTRUCTURES



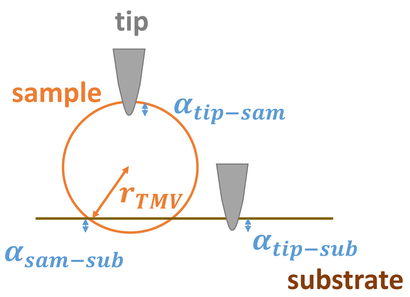


(16.5 ± 0.2) nm
mean value ± standard deviation



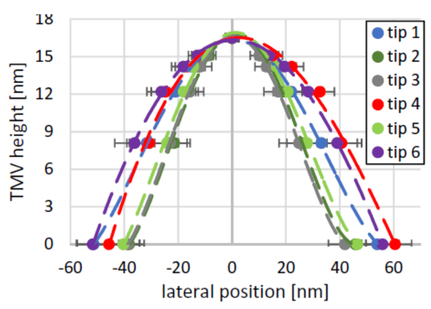


Interaction	Model	Deformation α [nm]
Tip-substrate (Si-mica)	Hertz (sphere-cylinder)	0.4
Sample-substrate (TMV-mica)	Chaudhury (cylinder-plane)	0.8
Tip-substrate (Si-mica)	Hertz (sphere-plane)	0.02



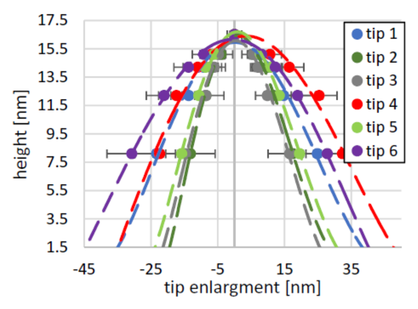
TOTAL TMV DEFORMATION $\alpha_{TOT} = \alpha_{tip-sam} + \alpha_{sam-sub} - \alpha_{tip-sub}$ = 1.2 nm

TMV DIAMETER $d = d_{meas} + \alpha_{TOT}$ = 17.7 nm



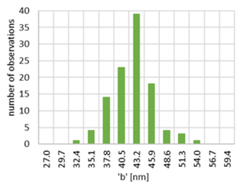
$X = a + b$
$b = X - a$

$enl = b_{left} + b_{right}$

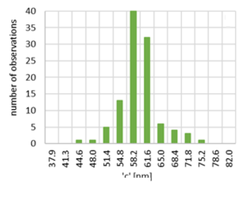


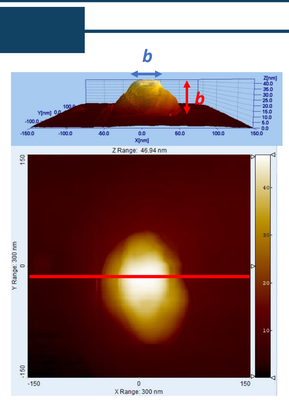
NON-SPHERICAL NANOPARTICLES

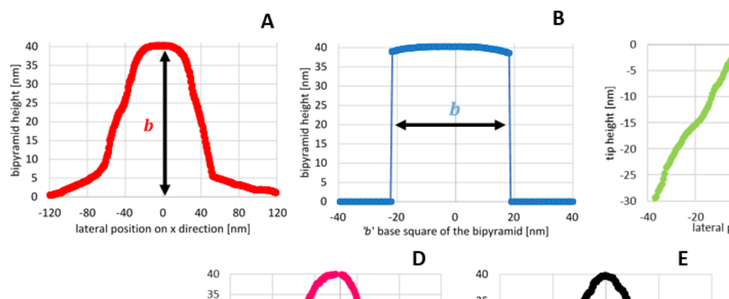
b = (43.2 ± 3.4) nm
combined standard uncertainty $u_c(b) = 1.7$ nm
effective degree of freedom $v_{eff}(b) = 80$
expanded uncertainty $U(b) = 3.4$ nm

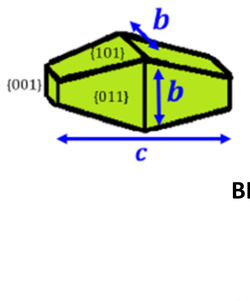


c = (58.2 ± 5.2) nm
combined standard uncertainty $u_c(c) = 2.9$ nm
effective degree of freedom $v_{eff}(c) = 200$
expanded uncertainty $U(c) = 5.8$ nm

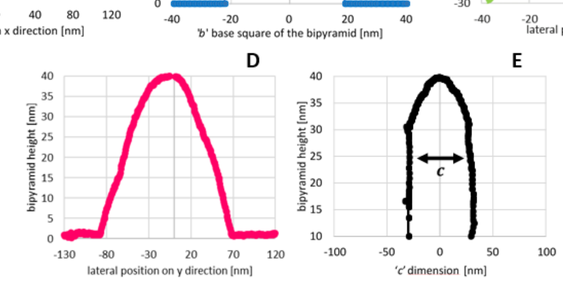


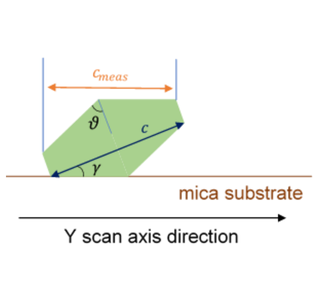




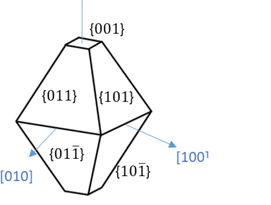


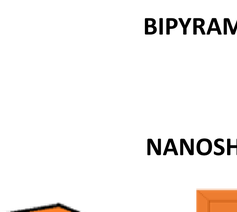
BIPYRAMID





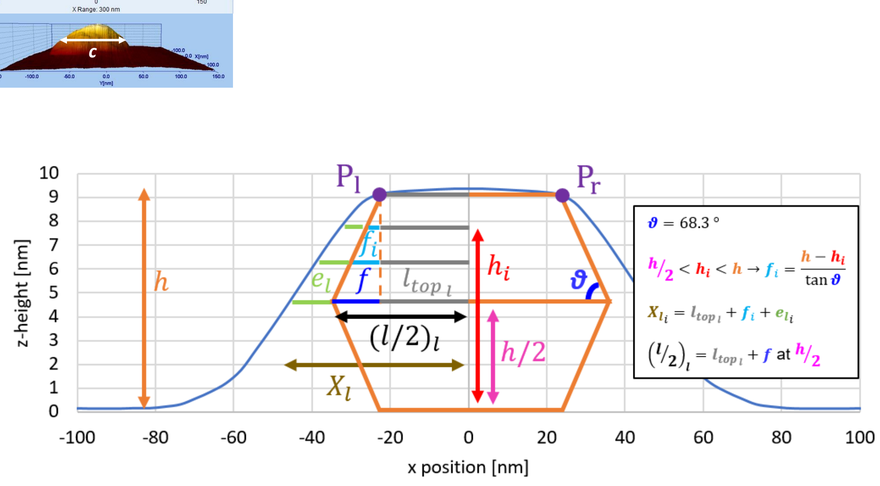
NANOSHEET

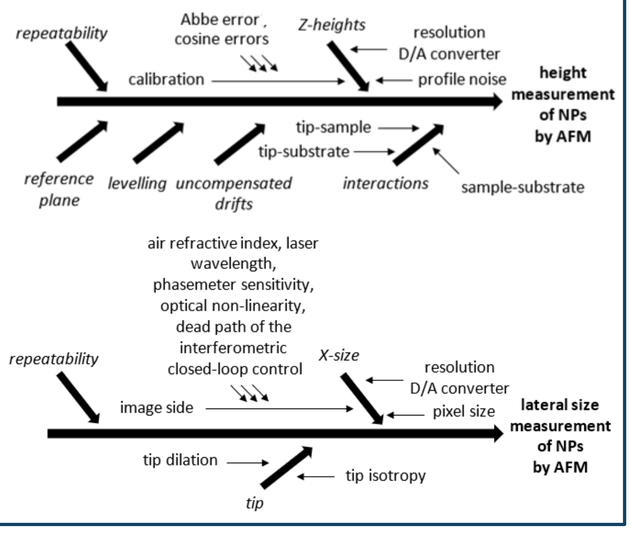




h = (9.4 ± 1.6) nm
combined standard uncertainty $u_c(h) = 0.9$ nm
effective degree of freedom $v_{eff}(h) = 180$
expanded uncertainty $U(h) = 1.8$ nm

l = (75 ± 26) nm
combined standard uncertainty $u_c(l) = 3.9$ nm
effective degree of freedom $v_{eff}(l) = 120$
expanded uncertainty $U(l) = 7.8$ nm





CONCLUSIONS

- Nanometrology plays a key role in nanoscience and nanomanufacturing, since it allows to produce traceable and accurate results, ensuring the quality of products down to the nanoscale.
- Tobacco Mosaic Virus, because its cross-sectional diameter has a stable value, it is used as a calibrator for reconstructing the dilation caused by the tip in lateral measures. Furthermore, its diameter is evaluated as the cross-section top-height from mAFM measurements corrected for the tip-sample-substrate interactions.
- Critical sizes of non-spherical NPs are reconstructed exploiting a geometrical approach based on intrinsic characteristics of the NP crystalline structure.
- Further developments will concern the creation of a new “mixed sample” containing isolated spherical and non-spherical NPs and bio-based nanostructures deposited onto mica substrate, in order to have the presence of both tip calibrators and reference materials in a single sample.

REFERENCES

[1] G. B. Picotto, M. Vallino, L. Ribotta, Tip–sample characterization in the AFM study of a rod-shaped nanostructure, Meas. Sci. Technol., 31 (2020) 084001 (12 pp), DOI: 10.1088/1361-6501/ab7bc2

[2] V. Maurino, F. Pellegrino, G. B. Picotto, L. Ribotta, Quantitative three-dimensional characterization of critical sizes of non-spherical TiO_2 nanoparticles by using atomic force microscopy, Ultram. 234 (2022) 113480 (13 pp), DOI: 10.1016/j.ultramic.2022.113480