Doctoral Dissertation
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Dimensional metrology at the nanoscale: quantitative characterization of nanoparticles by means of metrological atomic force microscopy

By

Luigi Ribotta

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Supervisor(s):
Dr. Massimo Zucco, Supervisor
Dr. Gian Bartolo Picotto, Supervisor

Doctoral Examination Committee:
Dr. Fabrizio Sordello, Referee, Università degli Studi di Torino
Dr. Gaoliang Dai, Referee, Physikalisch-Technische Bundesanstalt
Dr. Marco Pisani, Istituto Nazionale di Ricerca Metrologica
Prof. Gianfranco Genta, Politecnico di Torino
Prof. Renato Gonnelli, Politecnico di Torino

Politecnico di Torino
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Abstract

3D nanometrology supports nanoscience and nanotechnology through new standards and traceable methodologies of measurement and data treatment. The development of candidate reference nanomaterials for dimensional nanometrology will reduce uncertainties and improve traceability at the nanoscale. For this purpose, in my PhD project inorganic nanoparticles (NPs) and bio-plant viruses are studied using the INRiM metrological atomic force microscope (mAFM).

AFM topographies result from the dilation of the probe shape, the sample shape and the tip-sample-substrate interactions. Among other errors, accurate measurements of patterned surfaces and NPs are affected by errors due to probe shape and size. In order to reduce the uncertainty of measurements, the Tobacco Mosaic Virus (TMV) is studied as a tip characterizer.

Tip shape characterization is necessary for many applications, including dimensional, electrical, and magnetic measurements. TMV is chosen for characterizing commercial AFM tips because of (i) its simple geometry, (ii) its stable diameter, and (iii) its availability worldwide in nature.

The TMV is a cylindrical nanostructure with a circle-base diameter of about 18 nm as quoted in the literature by X-ray diffraction measurements, which represents a reference at the nanoscale. The diameter of the TMV is obtained from AFM images as the top height of the cross-section profile of isolated nanostructures. Since the mean diameter by mAFM is (16.5 ± 0.2) nm (smaller than the X-ray-based reference value), the tip-sample-substrate interactions are studied to correct the mAFM measurement and greatly reduce the deviation of the TMV top-height diameter by the mAFM and its reference value.

By assuming the TMV cross-section is undeformed, the tip shape is obtained from lateral measurements taking into account the enlargement, achieving a good repeatability for subsequent images.

Nowadays, quasi-spherical NPs are measured accurately by mAFM, through the determination of the mean diameter as the top-height of the cross-section profile. However, in most real-world, industrial nanomaterials have shapes that are much more complex than the spherical one. Non-spherical NPs represent a challenge regarding AFM measurements, because their particular geometries emphasize the limitations associated with finite tip size and shape.

Traceable measurement of non-spherical shapes and dimensions requires the development of new measurement methods. Through new geometrical approaches

which consider the nominal crystal structure and the conditions in which the TiO_2 particles have been synthesized, the critical sizes of bipyramids (~ 60 nm length × ~ 40 nm width) and nanosheets (~ 10 nm thickness × ~ 75 nm lateral) are robustly and accurately reconstructed by the mAFM images and data treatment. In this study, critical sizes like bipyramids breatdth and length, thickness and roughness of platelets, are quantitatively determined providing an uncertainty budget for each measurand. It is worth noting that the critical sizes of these NPs have resulted stable with low dispersion of values and with a monomodal distribution. It follows that they are suitable as potential candidate reference materials in dimensional nanometrology.

Pre-normative works on measurements of 3D nanostructures by AFM require a clear and unambiguous description of the sample to be measured with a consistent and easily understood terminology. The 'quality characteristics' that should be first regulated are intrinsic properties, *e.g.* critical sizes and shapes and descriptors. For this reason, non-spherical NPs characterisation included the quantification of morphological descriptors, that qualify the synthetized batches. In particular, bipyramids are described by shape descriptors, *e.g.* the elongation of about 1.4 indicates a perfect truncated shape, while nanosheets are described by roughness and texture parameters in order to qualify the anatase crystals synthetized.