



**E-MRS SPRING
MEETING 2021**

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COMPREHENSIVE CHARACTERIZATION OF AL-COATED TITANIA NANOPARTICLES WITH ELECTRON MICROSCOPY AND SURFACE CHEMICAL ANALYTICS



KEY PARAMETERS OF NANOMATERIALS ACCORDING TO REACH

What they are?

Identification	
Physico-Chemical parameters	
Composition: XPS,EDS	Size: EM
Crystallinity	Shape: EM
Surface Chemistry: XPS,ToF-SIMS	Surface Area

Where they go?

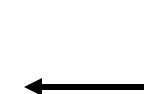
Behaviour
Solubility
Hydrophobicity
ζ-Potential
Dispersibility
Dustiness

What they do?

Reactivity
Biological (re)activity
Photoreactivity



Quantitative Structure Activity Relationships
Grouping, Read Across



REACH = registration, evaluation, authorization
of chemicals



HIGH QUALITY DATA

QSAR needs high quality data

- **Completeness:** complete physico-chemical characterization, including raw-, derived, and meta-data, SOPs for sample preparation, measurement and data reduction (FAIR)
 - **Relevance:** fit for purpose → meet the specific requirements
 - **Reliability:** compliant with GLP and/or standardized protocols (ISO, OECD guidelines, ...)
 - **Accessibility / Availability:** interchangeable, standards, FAIR principles
 - **Reproducibility:** standards, FAIR
- **FAIR** meets completeness, accessibility and reproducibility, but not relevance and reliability



KEY PROPERTIES OF THE METHODS

Complementary methods for comprehensive insights

Method	SEM	EDS	XPS	ToF-SIMS
Properties	Size, shape	Elemental composition	Composition, surface chemistry	Surface chemistry
Lateral resolution	1-2 nm	< 1 μm	> 1 μm	50 nm
Information Depth	A few nm	< 1 μm	10 nm	1 – 3 nm
Quantification	Length of projection dimensions	No quantification for single NPs	With suitable models	challenging
Detection limit	A few nm	0.1 at%	0.01 – 1 at%	ppb



SAMPLES

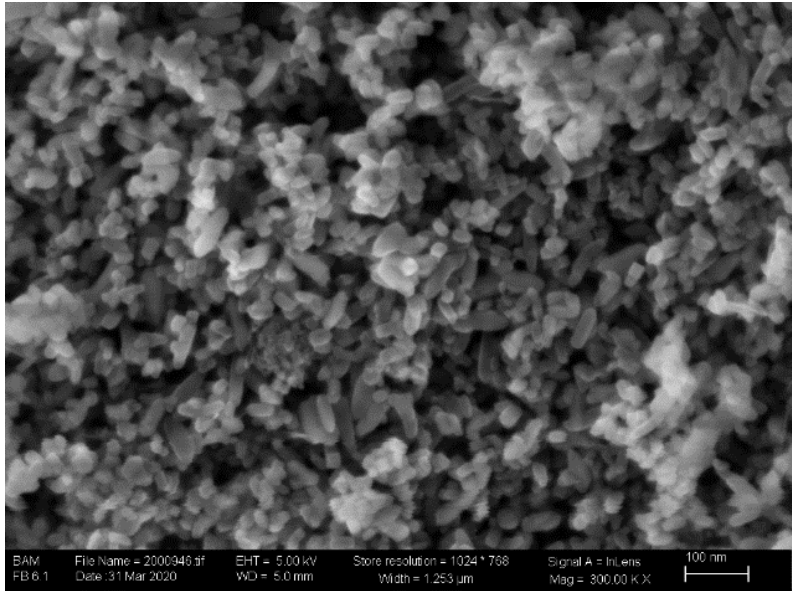
Samples from JRC repository representative for coated titania NPs

JRC ID	Material	Primary crystallite size /nm	phase	coating	hydrophobicity
JRCNM62001a	TiO ₂	21	rutile	Al ₂ O ₃	hydrophobic
JRCNM62002a	TiO ₂	21	rutile	Al ₂ O ₃	hydrophilic

Crystallite size from XRD



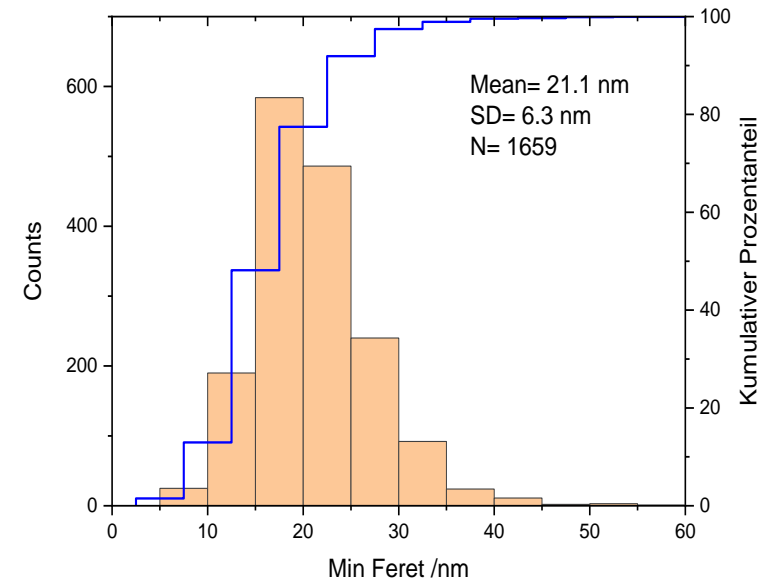
SEM: PARTICLE SIZE AND SHAPE



Elongated nanoparticles:
~ 20 nm * [20-50] nm

SE-InLens detector @ 5 kV
Prepared as dry powder on an Al sample holder
Full meta data: ISO/FDIS 20171

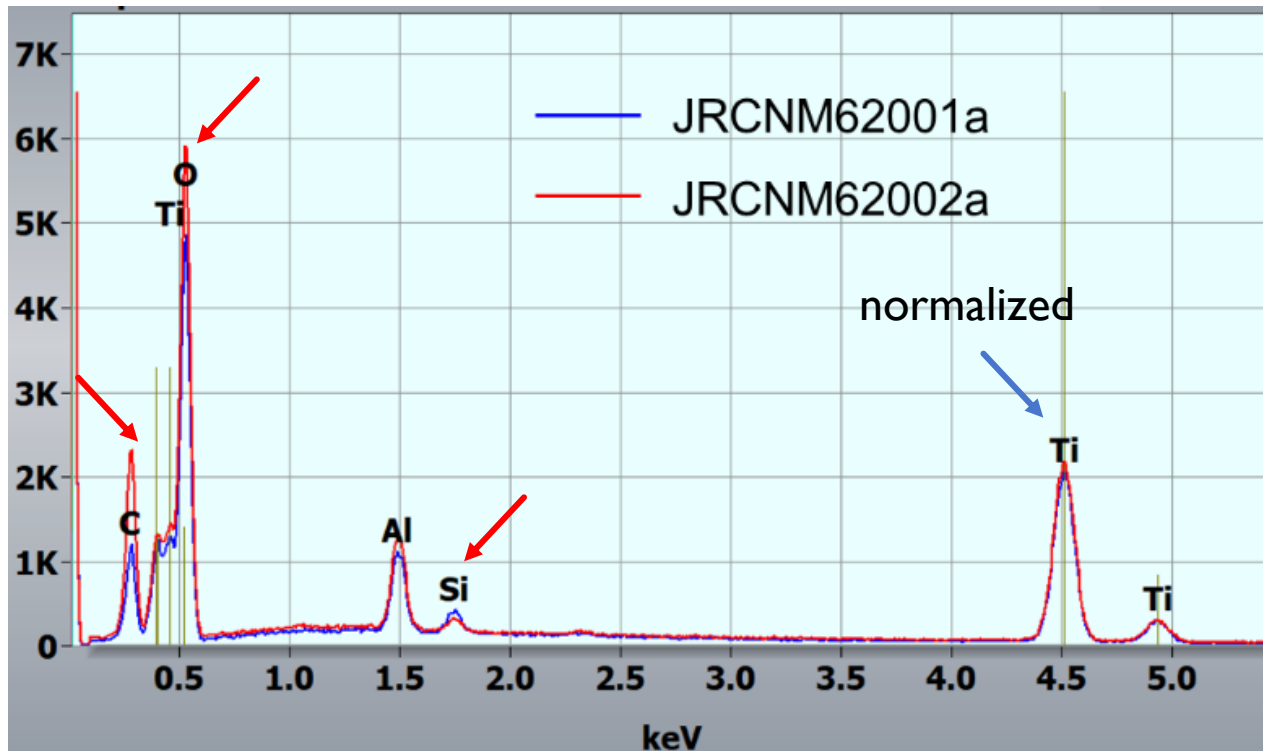
PSD (minimum Feret diameter)



Standards for the measurement of nanoparticle size and shape
TEM: ISO 21363:2020
SEM: ISO/DIS 19749



EDS: CHEMICAL COMPOSITION



Dry powder on silicon wafer

EDS: bulk analysis

No quantification algorithms for nanoparticle analysis available

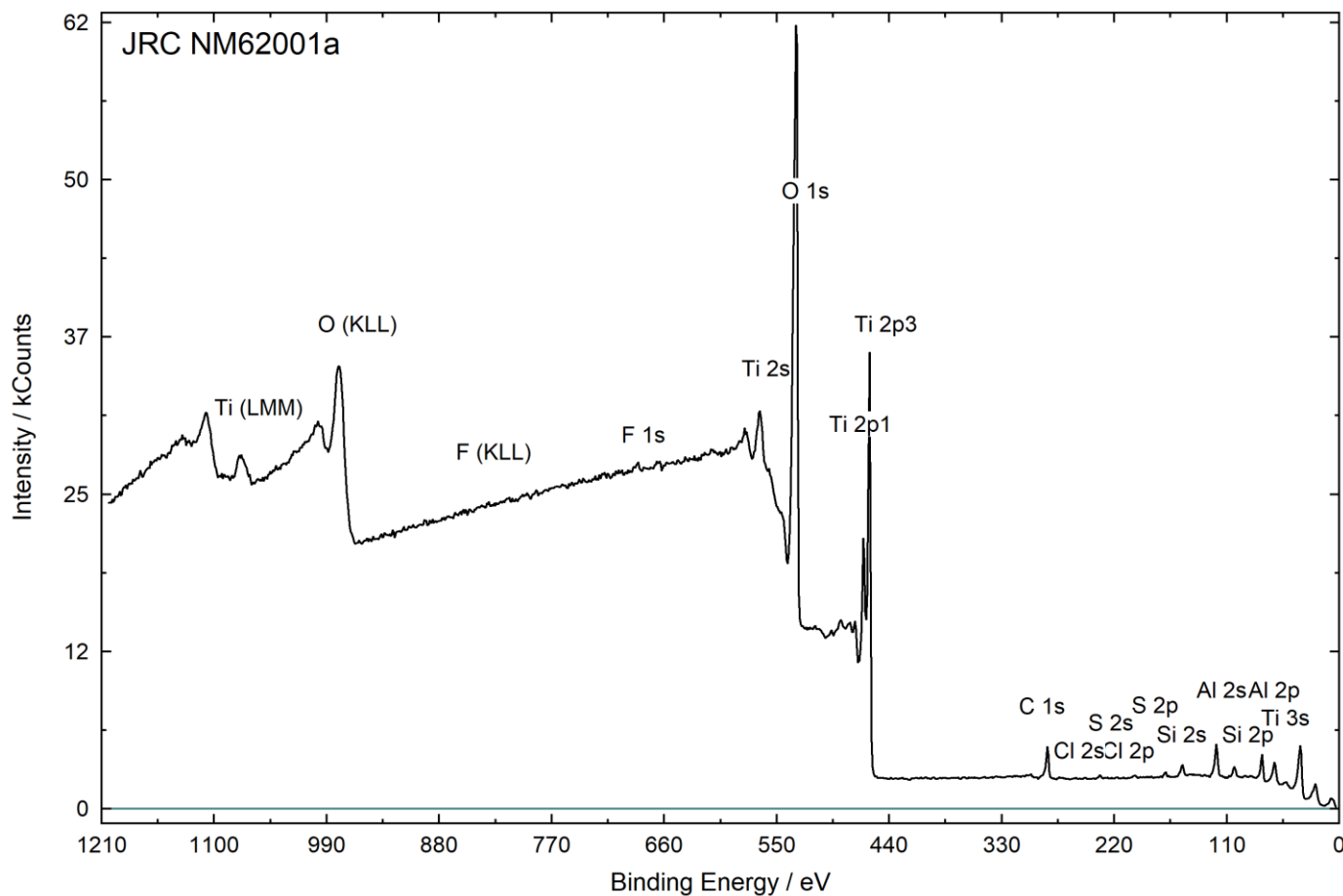
Valuable method for a quick **qualitative elemental** analysis and for a “more or less” comparison under the same measurement conditions

Performance and measurement standardized (ISO 15632:2012; ISO 22309:2011)

Data transfer standardized (ISO 22029:2012)



XPS: CHEMICAL COMPOSITION IN THE NEAR-SURFACE REGION



- All peaks (> 50 eV) must be assigned
- Criteria for clearly detected elements: S/N ratio > 3 ; more than one peak
- Distinguish between clearly detected elements (here: Ti, O, C, Al, Si) and probable elements (S, Cl, F)
- Charge referencing: ISO 19318
- Data format: VAMAS or ISO 14976:1998



XPS: QUANTIFICATION

62001a	O1s	Ti2p	Si2p	C1s	F1s*	Al2p	Cl2p*	S2p*
Experimental SF /at%	64.2	14.8	2.2	8.9	0.8	9.2	n.d.	n.d.
Theoretical SF /at%	62.9	16.1	2.5	7.2	0.5	10.8		
Rel. deviation / %	2.0	8.4	12.5	21.0	46.2	16.0		

62002a	O1s	Ti2p	Si2p	C1s	F1s*	Al2p	Cl2p*	S2p*
Experimental SF /at%	64.2	16.3	n.d.	7.8	0.6	9.7	0.4	0.6
Theoretical SF /at%	61.8	17.3	n.d.	7.5	0.4	11.8	0.4	0.8
Rel. deviation / %	3.8	6.0		3.9	40.0	19.4	0	40

Deviation similar or smaller to the relative uncertainty of 20 % which is usually estimated

Experimental SF:

- For each setup experimentally determined
- Usually provided by the manufacturer
- More precise

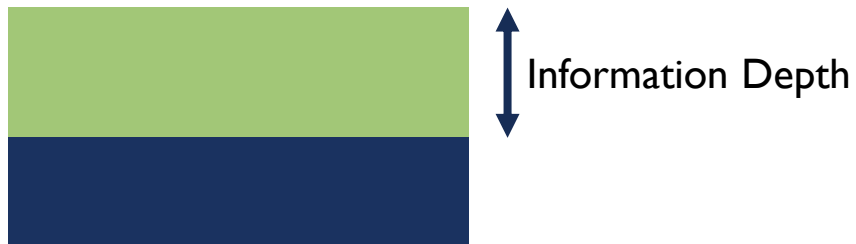
Theoretical SF:

- Theoretically determined (Scofield)
- Transmission function must be experimentally determined
- traceable



QUANTIFICATION OF NANO-OBJECTS

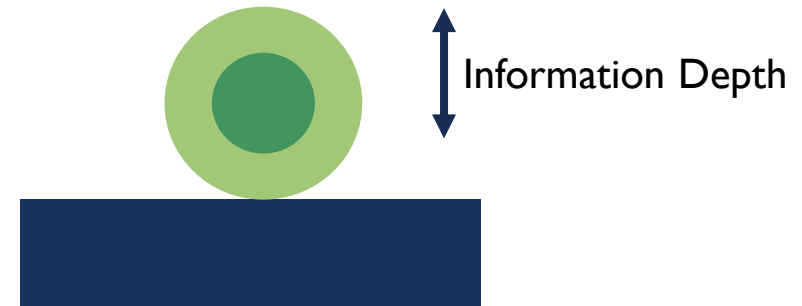
Usual quantitative model



Homogeneous material composition in the whole analysis volume

→ **Wrong model for nanoparticles**

Quantitative models for nanoparticles



Suitable models are available:

- $T_{NP} = \frac{T_{R \sim 1} + \beta T_0}{1 + \beta}$ (Shard, J.Phys.Chem.C 2012, 116, 16806)
- Numerical simulations: SESSA (NIST:SRD 100, vers. 2.1.1)
More information: ISO/TR 23173: Nanoparticle coating analysis by electron spectroscopy (will be published soon)

→ **Rough estimation with SESSA:**
Al₂O₃ shell of ~1 nm

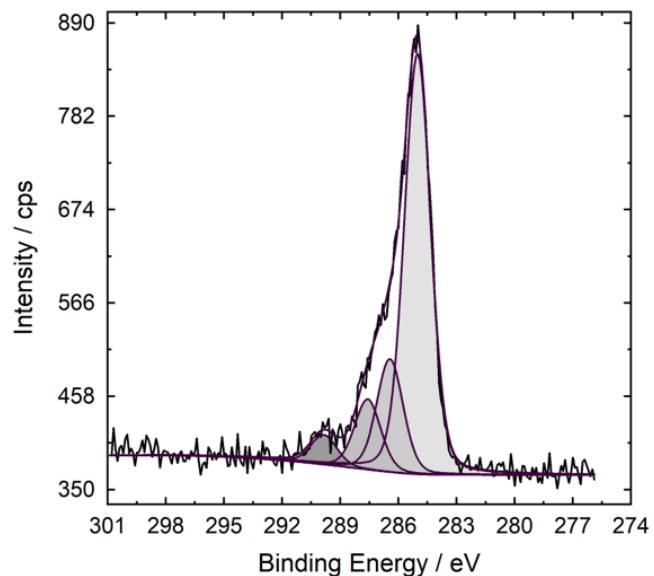


XPS: PEAK FITTING OF C1S FOR COATING (SURFACE CHEMISTRY)

62001a:

- Hydrocarbons, Si-C: 67%,
- O- containing functional groups: 33%

→ hydrophobic

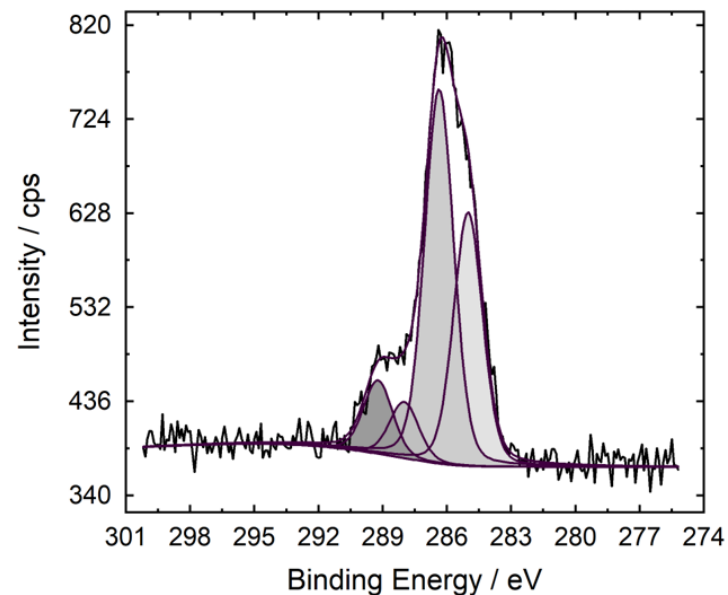


Peak name	Peak height/ cps	Lorentzian	Position/ eV	FWHM/ eV	abs. Area/ cps eV	rel. Area/ %
C-C, C-H	486.932	0.2	285.0215	1.6	897.55	66.34
C-O	130.945	0.2	286.4379	1.6	241.51	17.85
C=O	81.559	0.2	287.5883	1.6	150.46	11.12
O-C=O	34.418	0.2	289.8518	1.6	63.49	4.69

62002a:

- Hydrocarbons: 33%,
- O- containing functional groups: 67%

→ hydrophilic



Peak name	Peak height/ cps	Lorentzian	Position/ eV	FWHM/ eV	abs. Area/ cps eV	rel. Area/ %
C-C, C-H	259.102	0.2	285.0174	1.6	477.75	33.47
C-O	382.315	0.2	286.3706	1.6	705.23	49.41
C=O	57.474	0.2	288.0005	1.6	106.03	7.43
O-C=O	74.939	0.2	289.2236	1.6	138.23	9.69

Same FWHM and Lorentzian (peak shape) was used for all peaks



TOF-SIMS: SURFACE CHEMISTRY

Secondary Ions	Ratio 6200 I/62002
Ti ⁺	1.09
C _x H _y , aliphatic	0.70
C _x H _y , aromatic	1.47
siloxanes	135.00
Phthalate	0.58
C _x H _y O _x	0.7
SiO ₂ ⁻	18.08
SO ₃ ⁻	0.68

Normalized to Al⁺ and AlO₂⁻

- Ti detectable → thin (~ 1nm) or inhomogeneous Al₂O₃ layer
- Siloxanes and SiO₂⁻ at 6200 I a
- SO₃⁻ clearly detectable (from production process)
- Differences in hydrocarbons are not so clear (contamination effects ?)

Suitability of ToF-SIMS for nanoparticle analysis is subject of an ongoing VAMAS TWA 2 interlaboratory comparison



International Interlaboratory Comparison

Call for participants

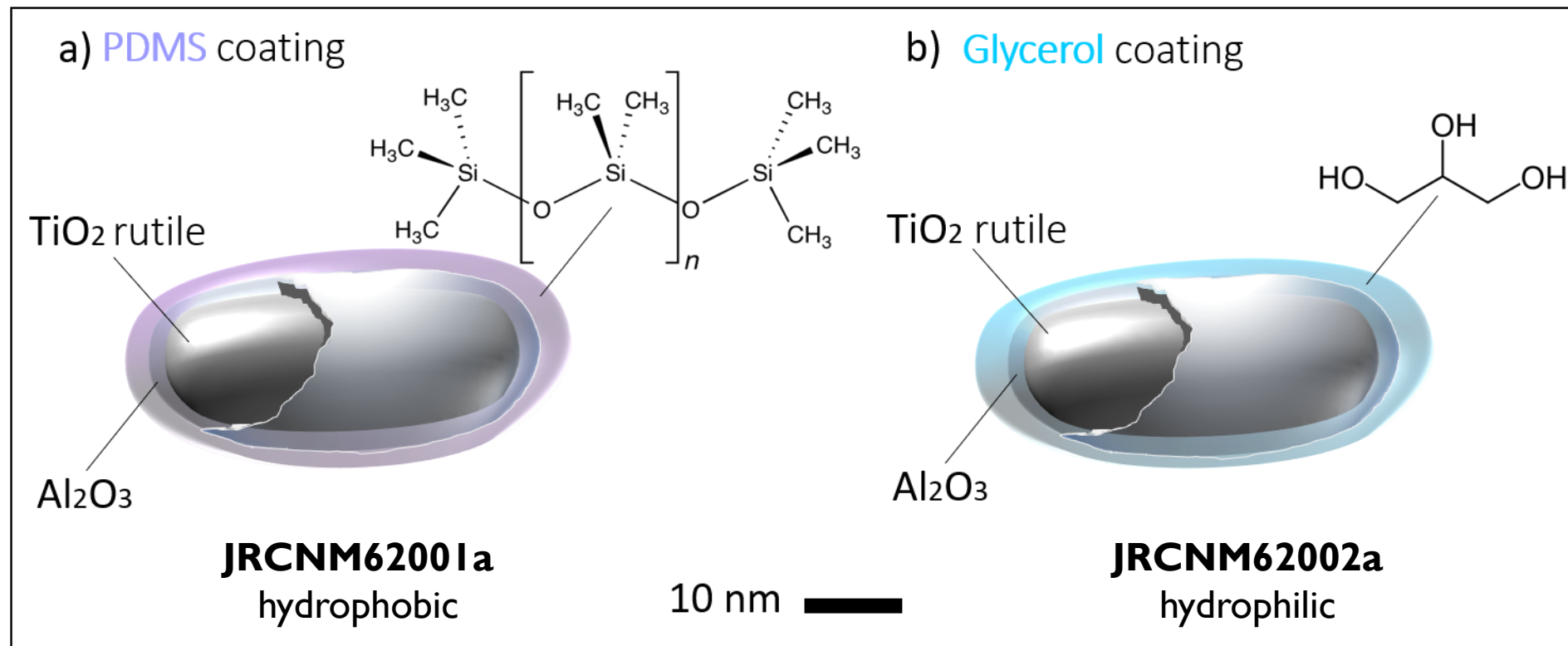
Secondary Ion Mass Spectrometry (SIMS)

Surface Analysis of Oxide Nanoparticles

Undertaken as part of VAMAS TWA 2 – Surface Chemical Analysis



RESULTS



ACKNOWLEDGEMENTS



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