The EC4SafeNano Project

- and the case study of Surface Chemical Transformations of Nano-TiO2 Samples upon Weathering

European Centre for Risk Management and Safe Innovation in Nanomaterials & Nanotechnologies

Background

To **ensure the sustainable production and use of nanotechnologies** is to understand and effectively control the risks along the industrial innovation value chain.

Knowledge about nanotechnology processes and nano-safety issues (hazards, fate, risk...) is growing rapidly but the **effective use** of this knowledge **for risk management** by market actors is lagging behind.

EC4SafeNano (*European Centre for Risk Management and Safe Innovation in Nanomaterials and Nanotechnologies)* **promotes** a **harmonized vision of expertise in risk assessment and management** for the public and private sectors to enable the safe development and commercialization of nanotechnology.

Work performed

- Map and analysis of the **needs and resources** of the market (regulators, industry, society, research, service providers...).
- **Develop a catalogue of harmonized services**: methods, guidance, studies, standards, training or certification, helpdesk, support for the development of national expertise centres...
- **Gathering the best available resources**, developing a governance structure, a business model, and operating procedures.

Proposed future offering services in nano-safety

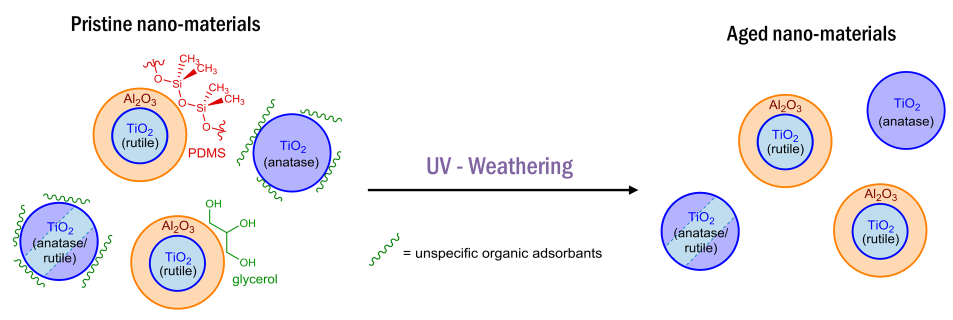
- Access to expertise / resources / facilities.
- Capacity building: skills and facilities.
- Education, training and certification programs.
- Good practice guides to assess and manage risks.
- Proposition of Toxicological Reference Values, of Occupational Exposure Limits (OELs) …
- (Support for) Open access databases: professional exposure, environmental levels …
- Feedback on research needs to improve the services.

EC4SafeNano is operated together by major European risk institutes with the support of numerous associated partners, gathering all stakeholders involved in Nanomaterials and Nanotechnologies (regulators, industry, society, research, service providers...).

Project duration: 01.11.2016 to 31.10.2019.
This project receives 2 M€ funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 723623

www.ec4safenano.eu/

Case Study – Surface Chemical Transformation



Background

Several case studies were performed in order to evaluate best practice and testing the business model and functionality of the centre.

Service: Physical-chemical characterization of nano-materials

Case study 2: Investigate the surface chemical transformations of representative nano-TiO_2 samples after UV weathering. In this case study the surface chemical transformations upon long-term UV irradiation of a representative set of titanium dioxide nanoparticles has been investigated. The materials have been analyzed by various analytical techniques. Each method addresses different aspects of the complex endpoint surface chemistry.

UV Weathering

Constant irradiation with variation of temperature and humidity, 125 cycles:

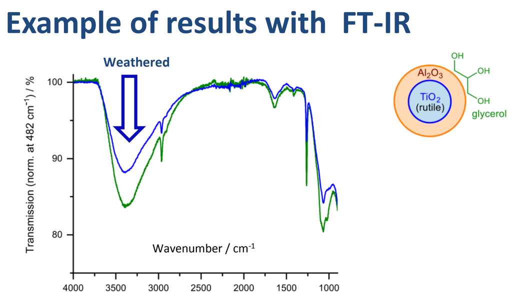
- The total irradiation was 1 000 h, which is equivalent to ca. 100 MJ/m².
- The average annual UV-Radiation for Central Europe: 180 MJ/m².

Duration /h	Temp. / °C	% Rel. Humidity
6	60	38
2	8	76

Samples

Brand Name	Producer	Crystalline Phase	Primary Particle Size	Surface Coating
UV Titan M262	Sachtleben	rutile	21 nm	Al_2O_3, PDMS
UV Titan M212	Sachtleben	rutile	21 nm	Al_2O_3, glycerol
P25	Evonic	anatase/rutile	15-24 nm	
NO-0058-HP	IOLITEC	anatase	22 nm	

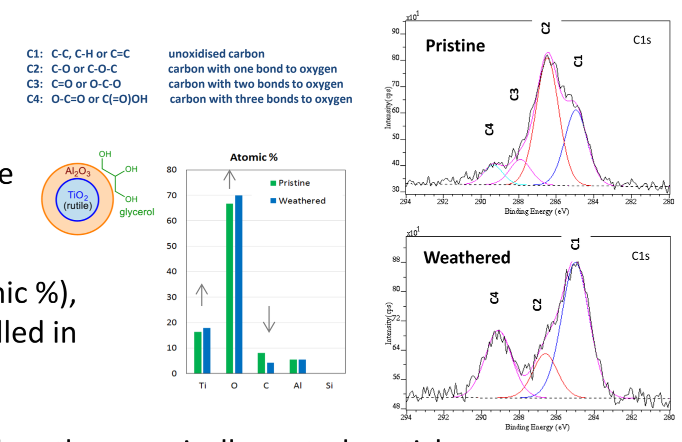
Example of results with FT-IR



Example of results with XPS (X-ray Photoelectron Spectroscopy)

Information depth: 2-5 nm. XPS is a straightforward method to **quantify the surface chemical composition** expressed in atomic %. Both the inorganic and organic coatings (PDMS, glycerol) can easily be detected and quantified.

The uncoated particles shows a surface amount of carbon (5-10 atomic %), which is at an expected level for mineral powders prepared and handled in normal air atmosphere before the XPS analysis.

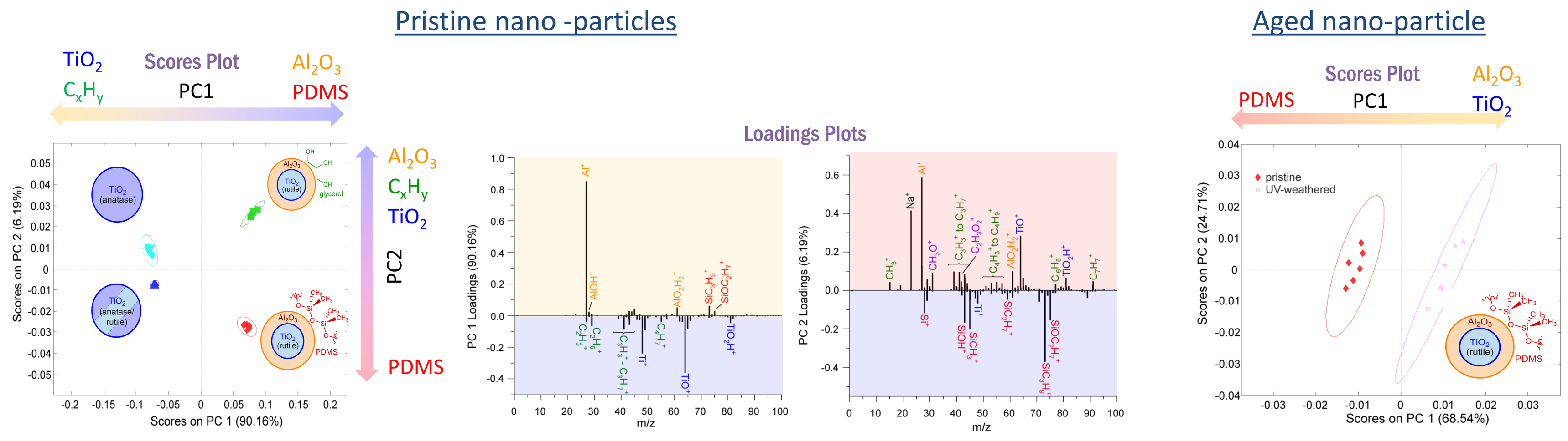


- ✓ The chemical states for carbon are very different for the uncoated vs. the organically coated particles.
- ✓ For the glycerol coated TiO_2, the elemental composition changes **after UV-weathering**. There is also **less C-O and more C-C and O-C=O** indicating a **preferential removal of glycerol and /or oxidation of glycerol.**

Examples of results TOF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry)

Information depth: < 1nm. TOF-SIMS results were analysed using Multivariate Data Analysis with Principal Component Analysis (PCA). PCA score quantifies the distance from the mean of all samples.

PCA of ToF-SIMS Positive Ion Mode data (negative ion mode not shown)



Conclusion

- To obtain a comprehensive picture, it is insufficient to concentrate on a single analysis technique.
- The XPS method quantifies the surface chemical composition and it is therefore straightforward to quantify nanoparticles surface chemistry, and follow any possible changes with ageing.
- By using ToF-SIMS in combination with PCA it was possible to identify even subtle changes in the surface chemistry of the investigated materials.
- A general trend that was observed for the UV-weathered samples is the decrease of organic material on the nanomaterial surface.
- No changes are observed for the Al_2O_3 layer and the TiO_2 core

Eric Johansson Salazar-Sandoval, Marie Ernstsson, Mikael Sundin, *RISE Research Institutes of Sweden*
Volker Wachtendorf, Valentin Kunz, Wolfgang Unger, *Bundesanstalt für Materialforschung und –prüfung (BAM)*

RISE RESEARCH INSTITUTES OF SWEDEN
Division Bioscience and Materials
Surface, Process and Formulation

CONTACT
Karin Persson, karin.persson@ri.se