PROJECT FINAL REPORT

Grant Agreement number: 604577

Project Acronym: SETNANOMETRO

Project Title: Shape-engineered TiO2 nanoparticles for metrology of functional properties: setting design rules from material synthesis to nanostructured devices

Funding Scheme: Collaborative project

Period covered: **from** 01/12/2013 **to** 03/03/2017

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Table of Contents

1 Final publishable summary report

1.1 Executive summary

According to European Commission [EC, COM (2012) 572, 3.10.2012], important challenges at European level are related to the establishment of validated method and instrumentation for production, detection, characterization and analysis of nanoparticles. In the framework of the SETNanoMetro project, the use of various measurement techniques for the determination of nanoparticles (NPs) properties has allowed to move from the currently used "trial and error" approach toward the development of well defined and controlled protocols for the production of TiO2 NPs. A particular care has been devoted to the establishment of correct metrological traceability chain for the determination of dimension and shape of TiO2 NPs..
The lack of international measurement standards for calibration is an aspect of particular relevance in nanotechnologies as it is difficult to select a universal calibration artefact to achieve repeatability at nanoscale.
The TiO2 NPs, produced in the project according to such procedures, were characterised and their properties were considered homogeneous to become candidate Certified Reference Materials (CRM) and used in various applications where the lack of metrological traceability is encountered.
The project results are expected to lead to fundamental impacts on the following areas:

- Environment: the increased knowledge of TiO2 NPs allows to improve the photocatalytic properties for the treatment of pollutants in air and water.
- Energy: the better knowledge of dimension and electronic structure of TiO2 allows to improve the traceability of Dye Sentitize Solar Cells (DSSC) measurements.
- Health: the engineering of topographic and surface composition of TiO2 nanostructured coatings of orthopaedic and dental prostheses supported the design of rules for the production of devices exhibiting optimized interfacial properties for a better and quicker integration of the implants in the hosting bone tissues.

A number of challenges were faced and solved to achieve the targeted breakthroughs in producing TiO2 NPs and to ensure metrological traceability and reproducibility of measurement results of the functional properties of interest. To do this SATNanoMeto has:

- pursued the preparation of sets of TiO2 NPs, each highly defined and homogeneous in bulk structure, shape, size, surface structure, to be used as such and/or in highly controlled and reproducible aggregated or assembled forms on proper supports.
- carried out an extensive and comprehensive metrological research devoted to the characterisation and production of standardised TiO2, that allowed the attainment of products with defined properties and sufficient homogeneity to be considered as candidate CRM. These candidate CRMs, suitable for assuring metrological traceability to measurement results, have been used for measurements under traceability conditions of operational performances in some selected, actual technological applications such as DSSC, toxicology related to orthopaedic and dental prostheses and photocatalysis.

1.2 Summary description of project context and objectives.

Titanium dioxide (TiO_2, titania) has been one of the most exploited semiconductor oxides in various technological fields for many years. This material has multisectorial application ranging from solar energy harvesting, photocatalysis for air and water remediation from pollution, production of smart materials with self-sterilizing, self-cleaning and superhydrophilic properties, healthcare sector for the development of implants or restoration materials with better prognosis, a longer durability and less failures.

These inputs are resulting in a flourish of both fundamental and technological studies devoted to titania, with a consequent increase in reports dealing with new functional behaviours and/or improved performances, with respect to what was previously known. Indeed, the number of papers dealing with TiO_2 that appeared in the scientific & technological literature has exhibited an impressive growth since 1990, as well as the amount of patents based on this material. However, it can be difficult to attain an objective and comprehensive evaluation of the impact of the proposed novelties, because of the wide heterogeneity of:

i) types of TiO_2-based NPs developed, each of them often exhibits a rich dimensional and morphological variety,
ii) surface and/or interfacial molecular states,
iii) assembly/aggregation states of the NPs to form nanostructured and nano-enabled systems,
iv) measurement conditions of the functional performances of these systems.

Moreover, in order to have NPs with engineered properties for specific applications, it is important to have flexible synthesis methods which can lead to NPs with different critical parameters (e.g. shape, crystallographic surface exposed) and critical dimensions.

With such scenario, one of the general objectives of the SETNanoMetro project was the evolution of TiO_2 NPs synthetic procedures from a “trial and error” approach to one based on the possibility to predict the properties of the engineered nanoparticles.

MODELLING AND FORMULATION OF STANDARD SYNTHETIC ROUTES TO SHAPE AND SIZE CONTROLLED TiO_2 NPs

A fundamental point will deal with the disclosure of the variables and parameters, and of the relationships among them, that rule the preparation of TiO_2 NPs with pure anatase or rutile crystal structure, exhibiting defined shapes, exposed surface facets and surface composition (WP1, WP2, in loop with WP4). The goal has been pursued by using different synthetic approaches:

- hydrothermal methods (HT)
- sol-gel methods (SG)
- an innovative approach represented by Laser Ablation on liquids (LA)

In particular, pursued shapes for anatase have been: square-based bipyramids, square-based prisms, and square-based platelets. Dimensions ranged from 20 nm to 200 nm. A scheme of ideally pursued shapes is shown in Figure 1.1.

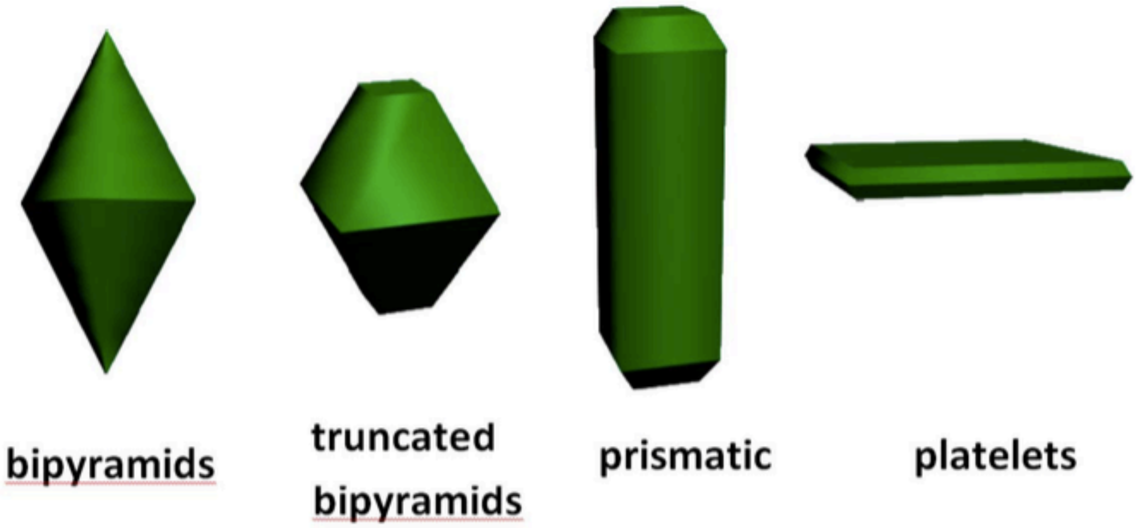


Fig 1.1 Ideal shapes of anatase TiO2 nanocrystals. The truncated bipyramid is the equilibrium shape in vacuum. Other shapes can be achieved by using shape controllers that adsorb selectively on a crystal facet, lowering its surface energy

The TiO2 based nanomaterials pursued in this project exhibit a defined geometry controlled by the lattice parameters and surface energy, enabling a new breakthrough in metrology of nanostructures.

METROLOGICAL CHARACTERIZATION OF SINGLE TYPE OF NPs

It was clear in this project that engineered TiO2 NPs present a complex and challenging system for measurement. To provide an adequate size-based metrological assessment of such samples, a number of factors have been considered.
- Firstly, it was important to determine the most appropriate measurand. For example, Critical Dimension (CD) in truncaded bypiramid was the height of the pyramids and the bases dimension of the pyramid. Playing with these dimesions has been possible to obtain the different shape depicted in fig 1.1
- Secondly, when the average particle size of the primary particles is measured, it is essential that the NPs system is adequately dispersed. This in itself is a non-trivial process and involved an independent study on each new sample encountered.
- Thirdly, it must be remembered that the addition of stabilizing agents to a sample in order to measure the primary particle size may change the state of the sample. This last point is particularly critical when considering risk assessment of engineered NPs in consumer products or for toxicological investigations.

In the project several fundamentally different measurement methods, like atomic force microscopy (AFM), dynamic light scattering (DLS), small-angle x-ray scattering (XRD), scanning electron microscopy (SEM) and scanning electron microscopy in transmission mode (T-SEM), were applied providing independent, reliable results of the selected measurands. Comparisons were carried out in order to verify the compatibility of these results. Each SETNanoMetro partner provided results and their measurement uncertainties.
Another innovative target of the project was constituted by the definition of standards for functional properties of TiO2 NPs, also in terms of the design of rules for reproducible and traceable measurements of surface and interfacial features defined at molecular level. To give some examples of the role played by these:

- surface hydroxy groups play a relevant role in the interfacial pathway of photocatalytic events;

- the size and location of the bandgap between the conduction band and the valence band of TiO2 is essential for the magnitude of the photocatalytic effect, and differ between e.g. crystal sizes;
- the effectiveness of the electron transfer from dye sensitizers to titania particles is significantly affected by the structure assumed by carboxylate moieties, the functional groups usually anchoring the dye molecules to the surface of TiO2 NPs, and this structure depends in turn on the local arrangement and electronic states of surface Ti^{4+} and O^{2-} sites;
- the fate of the interaction of an orthopaedic or dental prosthesis with the cells of the hosting tissue is ruled in a large extent by the causal sequence: (i) biomaterial surface structure, (ii) states of adsorbed water molecules, and (iii) states of adsorbed proteins.

In SETNanoMetro, particular attention has been payed to participate in and organize interlaboratory comparisons at both national and international level. To ensure that TiO2 NPs sample quality requirements were met, we proceeded as follows:

- TiO2 NPs sample stability was verified before, during and after the comparison. Verifications during the comparison were performed at regular intervals;
- several feedback loops were set up simultaneously among the project partners. An important part of interlaboratory comparisons and proficiency testings was dedicated to the determination of the result value of the measurand and its associated uncertainty.

OBJECTIVES

In the area, resulting from the intersection between nanoscience/nanotechnology and metrology, several issues are emerging, and among them the following have been recognized as relevant in the European Research Area.

- need for characterization of the relationship between measurable key parameters through the nanoscale to the higher order scales that provide new insight into the performance of nanostructured and nano-enabled material;
- interest toward the generation of reference information to test and optimise new design rules derived from length scale models;
- development of methods for measuring properties for which currently no methods exist, also ensuring the traceability, or at least the reproducibility, of existing methods;
- establishment of mechanisms to integrate new design rules to existing modelling techniques and apply these to industrially relevant materials and devices, delivering concrete results of industrial relevance (for example, the ability to design nano-coatings or nano-enabled coatings with specific performance properties).

2. Description of the main S&T results/foregrounds

2.1 Preparation of sets of TiO2 NPs with defined shape and size

In WP1 we pursued the preparation of sets of TiO2 NPs, each highly defined and homogeneous in bulk structure, shape, size, surface structure, to be used as such and/or in highly controlled and reproducible aggregated or assembled forms on proper supports.
The work carried out in WP1 lead to the development of soft models that give design rules for the synthesis of engineered TiO2 NPs with controlled size, shape, specific surface area and surface properties. The approaches used were three:

- hydrothermal methods (HT)
- sol-gel methods (SG)
- an innovative approach represented by Laser Ablation in liquids (LA)

Hydrothermal Synthetic Methods and NPs Availability
Anatase TiO2 NPs
The bipyramidal and prismatic anatase nanoparticles were obtained by an hydrothermal synthesis starting from a water soluble precursor (a complex of Ti and triethanolammine 1:2) purposely synthesized and triethanolammine as shape controller. The variables of the process (titanium precursor concentration, temperature, shape controller concentration and pH) were identified and their influence in the final nanoparticles size was analyzed by an experimental modelling. Changing the synthesis conditions it is possible to obtain bipyramidal or prismatic nanoparticles, moreover it is possible to modulate the size and the elongation of the particles.
The flat anatase nanoparticles (platelets) were obtained by a solvothermal synthesis starting from Ti(IV) butoxide as precursor and hydrofluoric acid as capping agent. Changing the synthesis conditions is possible to modulate the size and the thickness of the nanoparticles. A treatment procedure was developed in order to selectively remove the fluorine from the surface or from the bulk of the nanoparticles.
Figure 2.1.1 shows a summary of the anatase TiO2 NPs that can be offered. The developed HT synthetic procedure can be summarized as follows:
HT synthetic procedure able to lead to low-dimensional dispersity bipyramidal TiO2 anatase NPs, with low truncation along c-axis, then mainly exposing (101) type facets, (40 to 100 nm). (Figure 2.1.2)
HT synthetic procedure able to lead to low-dimensional dispersity bipyramidal TiO2 anatase NPs, with modulated truncation along the c-axis (platelets). (Figure 2.1.2)
HT synthetic procedure able to lead to low-dimensional dispersity prismatic TiO2 anatase NPs, exposing (100) and (101) type facets. (Figure 2.1.2)

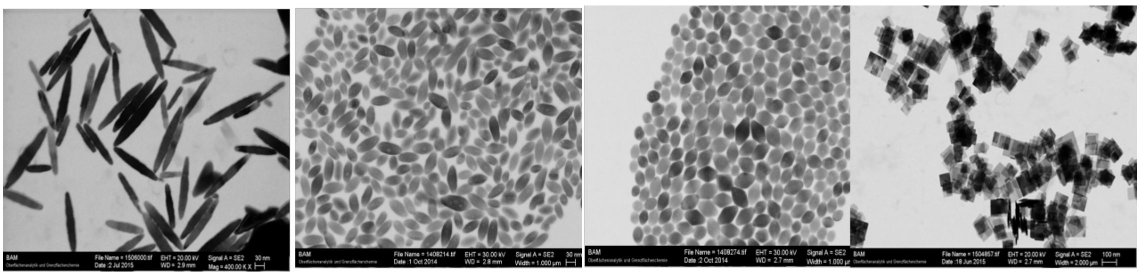


Figure 2.1.1 Examples of the variety of TiO2 Anatase NPs obtained by HT method in the SETNanoMetro Project: from prismatic to platelets.

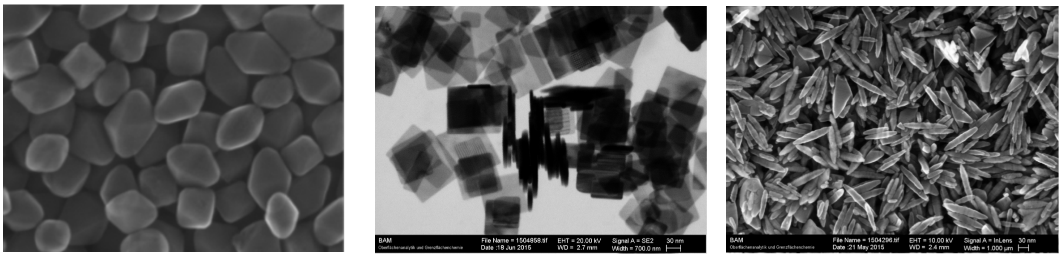


Figure 2.1.2 Examples of the variety of TiO2 Anatase NPs obtained by HT methods in the SETNanoMetro Project: prismatic platelets and nanorods

Rutile Nanoparticles

Hydrothermal synthesis conditions for ensembles of prismatic rutile NPs were developed, with the procedure to modulate the shape factor and length along the c-axis. A variation of the length along c-axis between 150 nm and 1500 nm was obtained, with shape parameters ranging from 2.5 to 6. These sets of NPs have a relevant and predictable percentage of {110} facets. Typical results are reported in 2.1.3.

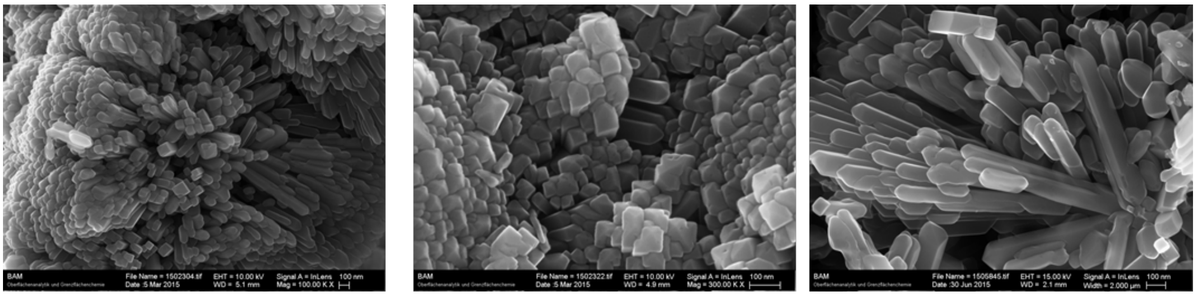


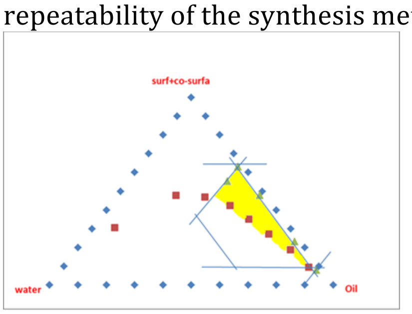
Figure 2.1.3 Examples of Rutile TiO2 NPs.

Sol Gel Synthetic Methods and NPs Availability

The sol-gel route is a versatile technology for obtaining TiO2 NPs with controlled crystalline ratio, surface area and sizes and one of the most interesting because of its simplicity, cheapness and high quality of final products. In SETNanoMetro project, two type of NPs were targeted:

- TiO2 anatase nanoparticles with optimized size <20nm
- TiO2 anatase nanoparticles with high specific surface area (>150 m^2/g)

The low size anatase nanoparticles were obtained by water in oil (W/O) microemulsions, specifically, through reverse micelles microemulsions. The most significant variables of the process (water, oil, surfactant/co-surfactant concentration, Titanium precursor concentration and its ratio with respect to the water content, Sintering temperature and time) were identified and their influence in the final nanoparticle's size were analyzed by an experimental modelling. In the Fig. 2.1.4 the area of the ternary diagram is shown, where the size of nanoparticles are between 8 nm and 20 nm. A good repeatability of the synthesis method was observed.



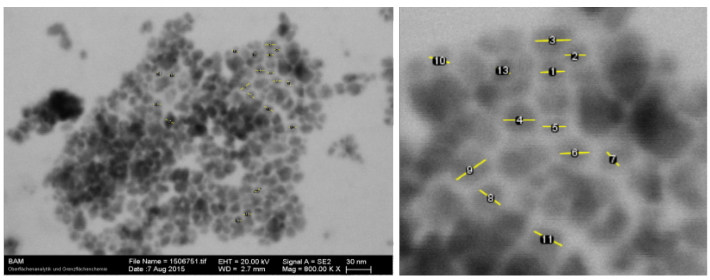


Figure 2.1.4 Ternary diagram of the microemulsion F igure 2.5 TSEM micrographs of the TiO2 nanoparticles lowerby sol-gel .

The TSEM micrographs, carried out by BAM, of the obtained nanoparticles are shown in Figure 2.1.5. The anatase TiO2 nanoparticles with high specific surface area were synthesized by a conventional sol-gel route. Many parameters including precursor, solvent type, solvent molar percent, water molar percent, reflux temperature, reflux time, sol drying method, calcination temperature and extraction-crystallization process were modelling to achieve the best synthesis process for titania nanoparticles with specific surface area of 163 m^2/g and assize of 6-13 nm. Figure 2.1.5 shows the characterization of TiO2 NPs by SEM ant TSEM carried out by BAM.

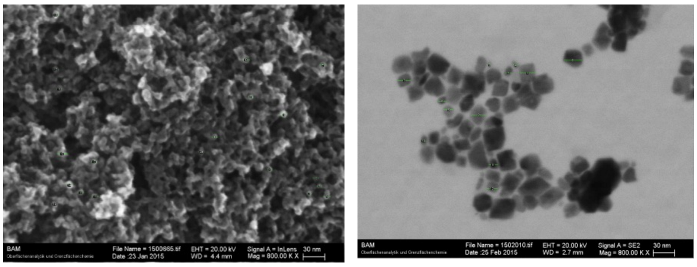
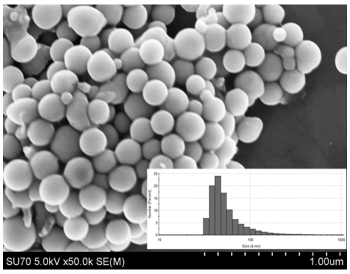


Figure 2.1.5 SEM and TSEM micrographs of TiO2 nanoparticles with a specific surface area of 163m²/g synthesized by sol-gel.

Laser Ablation Synthetic Methods and NPs Availability



The use of pulsed laser ablation (LA) on solid Ti plate (99.99%) targets in liquids (water, also in the presence of surfactants as shape controllers) led to the set up of procedures able to provide spherical anatase TiO2 NPs with controlled diameters between 25 nm and 100 nm. A typical SEM micrograph of these NPs is reported in Figure 2.1.6.

Figure 2.1.6 Spherical anatase TiO2 NPs obtained by Laser Ablation of Ti target in water.

TiO2 NPs commercialized by SETNanoMetro

The final output of SETNanoMetro regarding shape and size controlled TiO2 NPs is:

1. bipiramidal TiO2 anatase NPs with low truncation (30 nm - 100 nm hydrodynamic diameter), main surface exposed (101)
2. elongated TiO2 anatase NPs with shape parameters from 2 to 6, main surfaces exposed (101) and (100)
3. TiO2 anatase nanoplatelets with shape parameters from 0.15 to 0.30, main surfaces exposed (001) and (101)
4. Prismatic rutile NPs with length from 150 to 1500 nm and shape parameters from 2.5 to 6
5. Sol-gel TiO2 NPs with diameters < 20 nm
6. high surface area sol gel TiO2 NPs (specific surface area > 150 $m^2\ g^{-1}$)
7. spherical TiO2 NPs from LA

The NPs can be purposely synthesized with the size and shape desired within the limits indicated above.

2.2 Modelling of the synthesis of TiO2 NPs

The proposed and achieved WP2 objective was the modeling of the processes for TiO2 NPs obtained by hydrothermal (HT) and sol-gel (SG) synthesis in view to predict process evolution and end product reproducible targeted characteristics.

As leader of WP2, RD was involved in the modelling activities, having as partners UNITO and IK4 TEKNIKER, which supplied the experimental data obtained in WP1, regarding anatase nanoparticles synthesis by hydrothermal and respectively sol-gel routes. Thus, a fundamental project point dealt with the theoretical modeling (WP2) in loop with the experimental activities of synthesis (WP1) and characterization (WP1 and WP4) performed by the partners UNITO, TEKNIKER, BAM and INRIM, in view to disclose the variable parameters and properties, and the relationships among them that rule the preparation of TiO2 NPs with pure anatase crystal structure, defined shapes, size and surface. This interplay between WP2, WP1 and WP4 and the modeling methodology is shown in the Figure 2.2.1

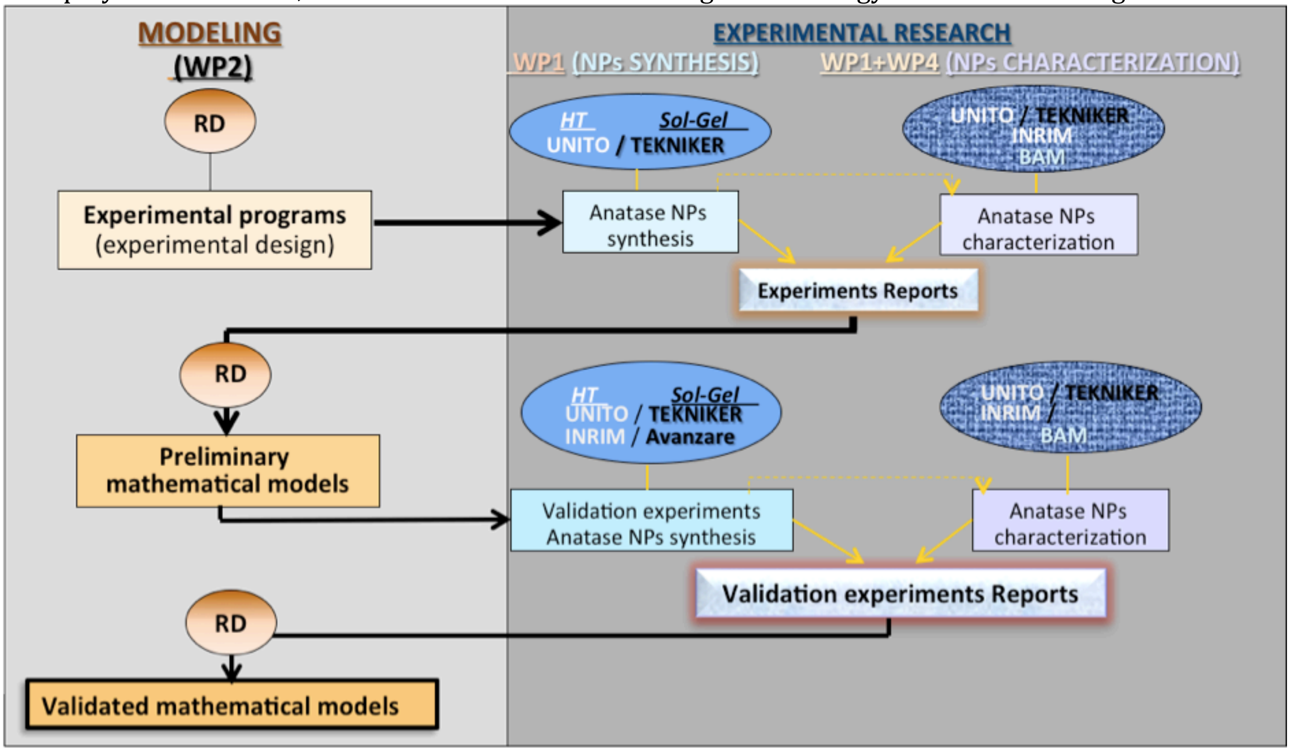


Figure 2.2.1 Modeling and experimental research interplay

The modeling specific objectives, targeted to predict the characteristics of different NP types obtained by HT and SG synthesis and the applied modeling methods, are shown in Figure 2.2.2. The modeling methods were chosen to be suitable for the number of process parameters, their interaction during the synthesis processes and their influence on the end product characteristics.

The approach consisting of the use of different modeling methods for the same shape controlled anatase NP type obtained by hydrothermal synthesis, proved through the validation experiments that the computed outcomes with the developed models (i.e. experimental design and multiscale models applied for truncated bipyramids and prisms), are close - whichever modeling method is used, being also close to the experimental data.

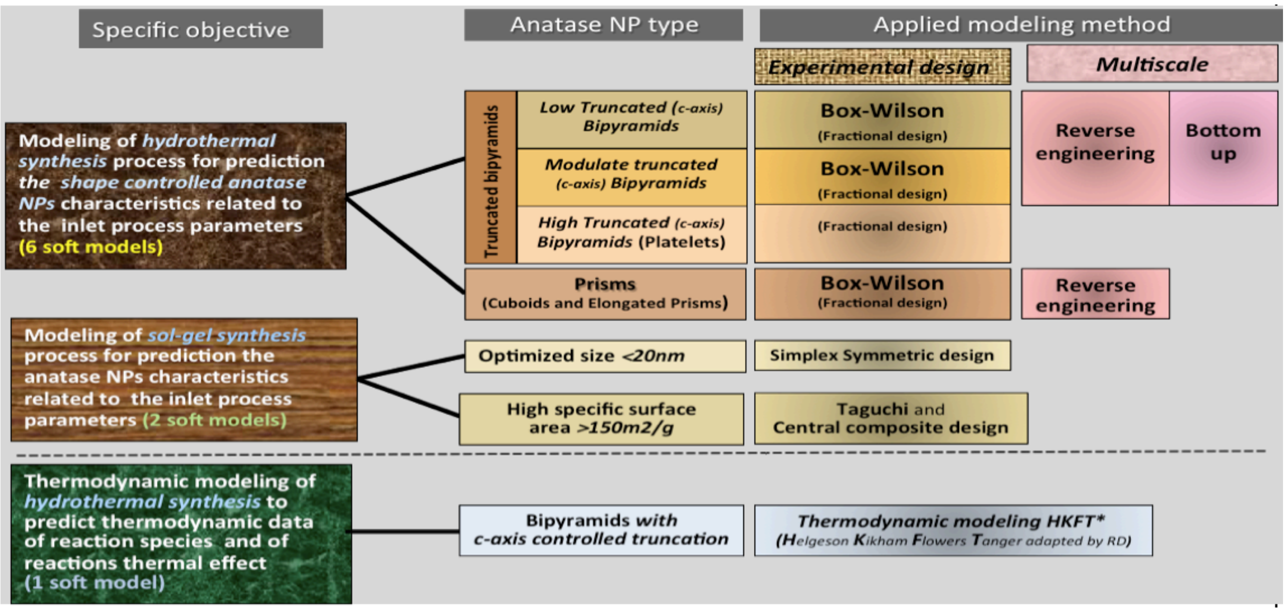


Figure. 2.2.2 WP2 specific objectives and applied modeling methods

The main S&T results of WP2 are:
- 9 SOFT MODELS for prediction the characteristics of anatase NPs obtained by HT and SG synthesis, related to relevant process parameters (4 of the models are WP2 milestones: MS 5, MS 6, MS 7, MS 8).
The developed mathematical models (soft models) are:

No.	Developed mathematical models	MS/TRL
1	Experimental design soft model for hydrothermal synthesis of bipyramidal anatase NPs with low truncation along c-axis (Y3*≈1.5) and elongated prisms (Y3*= 1.8-5.5)	MS 5/ Provided TRL 2 Achieved TRL 3
2	Experimental design soft model for hydrothermal synthesis of bipyramidal anatase NPs with modulate truncation along c-axis (Y3*≈1.3)	MS 6/ Provided TRL 2 Achieved TRL 3
3	Experimental design soft model for hydrothermal synthesis of prismatic anatase NPs (cuboids with Y3*=1.3)	
4	Experimental design soft model for hydrothermal synthesis of bipyramidal anatase NPs with high truncation along c-axis (platelets Y3*≈0.12–0.29)	
5	Experimental design soft model for sol-gel synthesis of anatase NPs with low size (< 20nm)	MS 7/ Provided TRL 2 Achieved TRL 3
6	Experimental design soft model for sol-gel synthesis of anatase NPs with high specific surface area (>150m²/g)	
7	Reverse engineering soft model for hydrothermal synthesis of shape controlled anatase NPs (based on artificial neural network and genetic algorithms)	
8	Bottom-up soft model for hydrothermal synthesis of bipyramidal anatase NPs with modulate truncation (referring to crystals birth and growth in HT process)	
9	Thermodynamic soft model for hydrothermal synthesis of bipyramidal anatase NPs with modulate truncation (for computing the properties of reaction species and the thermodynamic functions in process conditions)	MS 8/ TRL 2 (Provided and achieved

* Y3= shape parameter (average ratio between a and c dimension of the NPs)
- DATA BANK of process conditions for synthesis of anatase NPs with predicted characteristics was built with data experimentally obtained and computed with all the developed soft models.

In the data bank tables, the process conditions giving the relevant shape and size controlled characteristics of each type of anatase NPs developed in the project are selected. From these data, it results that NPs with almost the same characteristics could be obtained with different combinations of process parameter values. This aspect is well revealed by the diagrams from the Figure 2.2.3 referring to the shape and size of bipyramidal NPs with different truncation obtained by HT synthesis, at different process parameters (pH and temperature). Thus, it could be seen that the good operating conditions are not unique and also that the developed models could be used as tools for prediction and control of the NPs shape and size, because they give the correlation between certain product characteristics and the combinations of process parameters.

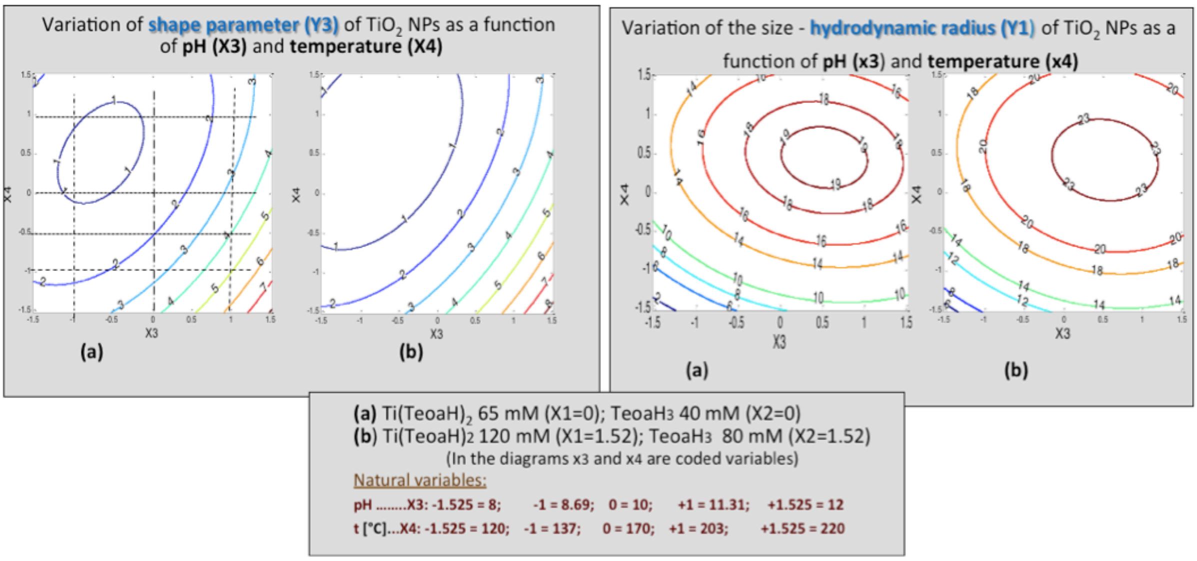


Figure 2.2.3 NPs shape and size control using different combinations of process parameters value

In WP8, the partner used, with good results, some combinations of optimal process parameters from the data bank, for the scale-up of sol-gel and hydrothermal syntheses.
In DoW the foreground for dissemination of WP2 was not provided, because WP2 work was strictly correlated with that of WP1 and WP4 for the synthesis experiments and NPs characterization. Nevertheless, the scientific results obtained through partners cooperation allowed RD to participate in dissemination activities (2 papers and 2 communications at project Erice workshop).
Through its close interplay with WP1 and WP4 work, modeling was a tool which contributed to the evolution of the preparation of predictive engineered TiO2 anatase NPs, from a “trial and error” approach to knowledge – based one, both at project beginning, by designing the experimental programs of WP1 for each synthesis route and each type of anatase NP, for the systemic investigations in the experimental research and optimization its time and cost, and finally, by processing the experiments data and development of mathematical models - soft models that can be used as design rules for synthesis of anatase NPs with defined and reproducible shape, size, surface, these specific characteristics being targeted for certain uses, well defined in the project, as energy (solar cells -DSSC type), environment (photo-catalysis in reactors for toxic effluents cleaning), health (nanocoatings for medical devices) and metrology (candidates of reference materials).

2.3 Assembly and aggregation of TiO2 NPs on proper supports

The thickness and physic-chemical characteristics of TiO2 coatings can greatly influence their final performance. In SETNanoMetro, different deposition procedures were set for applying films of TiO2 NPs with defined and homogeneous thickness on supports of interest for the application studied into project. The selected substrates were the following (in the Figure 2.3.1 from left to right):

- Silica glasses for photocatalytic measurements
- Conductive glasses (FTO) for dye-sensitized solar cells
- Ti-alloys for orthopedic and/or dental prostheses, for cell cultures.

Since it was found to be quite laborious to polish the Ti-6Al-4V substrates, a number of alternative substrates in the shape of Ti-coated glass slides was produced by Plasma Vapour Deposition (PVD).

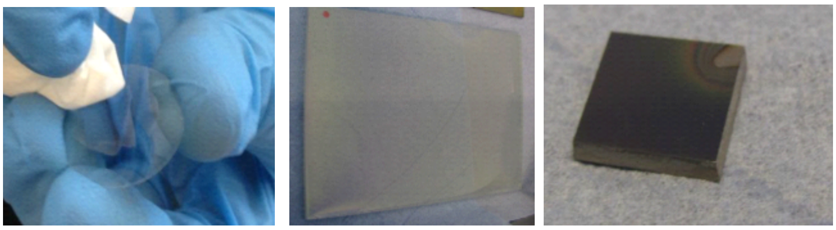
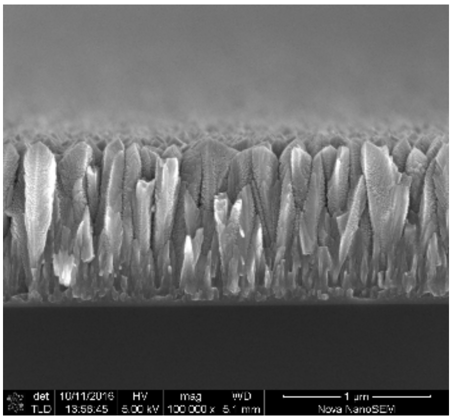


Figure 2.3.1 Substrates selected for the deposition of the coatings

The different film deposition procedures studied within the project were:

- Direct formation of films by using PVD sputtering and screen printing methodologies.
- Sol-gel technologies and conventional methods using TiO2 NPs (commercial and synthesized in the project).
- Self-assembly of TiO2 NPs in multiple layers (layer by layer deposition).
- Formation of films of TiO2 using PVD sputtering



As a result of the project PVD coatings of well-defined crystallinity (rutile, anatase and mixtures hereof) have been developed. A window of homogeneity was established and good batch to batch reproducibility was obtained. Furthermore, the heights in the deposition chamber resulting in a homogeneous sample thickness were carefully investigated. In addition, to perform and optimiz the PVD deposition process, basic analysis (SEM – Figure 2.3.2), XRD and measurements of photocatalytic activity of the CO_2 generation originating from acetone degradation) on the PVD TiO2 coatings were done.

Figure 2.3.2. SEM micrograph of anatase TiO2 coting deposited by PVD

Formation of film of TiO2 fabricated by screen-printing

The choice of the right processing methods is crucial to increase the global efficiency and reduce the manufacturing costs of photovoltaic devices. In general, processing methods should allow the control of the main parameters of the deposited layer like morphology, thickness or geometry. These parameters were fine-tuned during the SETNanoMetro project in order to lead to the fabrication of an optimized device.

Screen-printing was considered for the deposition of the anode material. Screen-printing is a method that allowed us to optimize titania layer and to fine tune it depending on the targeted application. The layer thickness and its porosity are crucial for industrial applications where reproducibility is important for the success of the process. The relation between the ink concentration and the mesh type used for the printing process was studied, is now known and allows adjusting the layer thickness precisely. Porosity is in close relation with particle shape or size and sintering conditions of the resulting layer. A good compromise between porosity, surface area and efficiency was found using 18h heating time during hydrothermal growth.

Based on the optimized method to produce titania films with the required quality for dye solar cell applications, thin films of TiO2 nanoparticles, with defined size and shape produced in the project, were fabricated, on conductive glasses, by screen-printing technique with optimized thickness and porosity.
Titania nanoparticles were successfully incorporated into the organic binders and converted in printable ink. This ink was formulated to follow several requirements:
- The final viscosity should be compatible with the process
- Templating agents are incorporated in order to improve the layer rheology
- The dispersion of nanoparticle should be stable over the time

When using the optimum formulation, the use of two different processes allowed to improve the nanoparticles dispersion and reduced aggregation in order to get the best layer quality, which could be used in dye solar cells. All the printed layers were characterized using SEM (Figure) and used by the project partners.

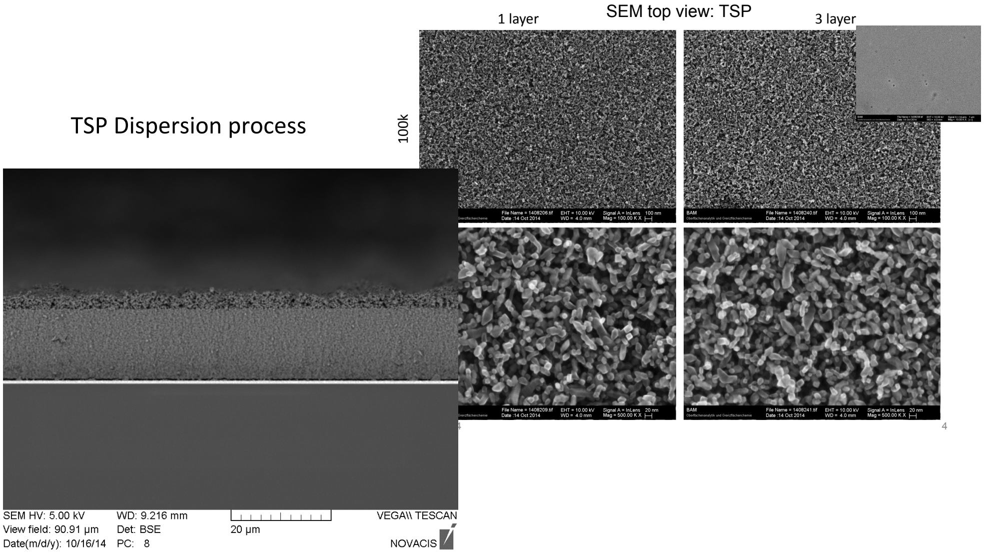


Figure 2.3.3. Example of SEM cross-section and top view of TSP layer (ink obtained by dispersion process)

Formation of film of TiO2 NPs by using sol-gel technology

As the supports and NP's functionalization was very challenging in the project, it was decided to use a sol-gel formulation to promote the adhesion of the NPs synthesized during the project to the supports and to slightly stick nanoparticles between them. The amount of sol-gel reactant was optimized with respect to the NPs concentration to maintain the porous structure between the nanoparticles.
For the preparation of mesoporous and mesostructured TiO2 anatase films obtained by using the NPs prepared in SETNANOMETRO two depostion technique were employed; dip-coating and spin-coating. By using spin-coating, thin layers were obtained (between 250 and 450 nm for coatings prepared with 1 or 3 layers, respectively). The dip coating deposition technique was employed for the controlled deposition of films with higher thicknesses, between 500 nm – 10000 nm as a function of the number of applied layers and the TiO2 concentration in the starting sol-gel solution. These coatings were deposited onto the 3 substrates of the project, and characterized by SEM as it is shown in the
Figure 2.3.4

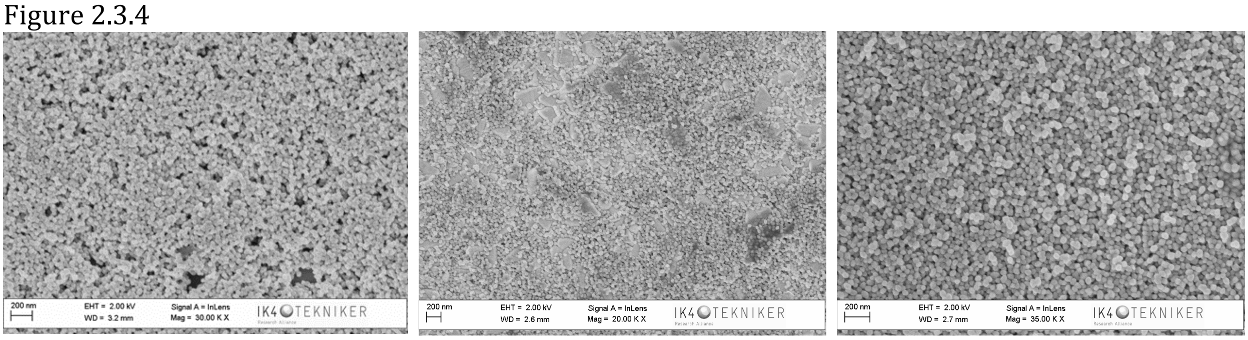


Figure 2.3.4. TiO2 coatings deposited onto different substrates by dip-coating technique

Formation of supported films by self-assembly of TiO2 NPs

For the controlled assembly of TiO2 NPs, the layer-by-layer deposition method was selected. This technique of thin film fabrication consists of the deposition of alternating layers of oppositely charged/functionalized materials with wash steps in between. The technique offers an easy control over the film thickness and is a simple and inexpensive means for film preparation. In addition, one of the pros exhibited by this method is the stability of the functionalized surfaces when exposed to ambient air. However, the controlled assembly of TiO2 NPs on the surface of the selected supports requires a proper functionalization of the supports which will be employed in order to promote the adhesion of the film to the substrates. In this way, the functional groups on the substrates should react with the functional groups of the functionalized nanoparticles deposited on them. The strategy to be followed can be seen in Figure 2.3.5.

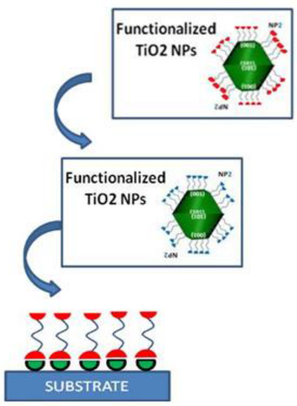


Figure 2.3.5. Strategy for films preparation by layer-by-layer deposition of functionalized NPs

In a first step, the two different functional groups to be attached to the NPs were selected: amine and aldehyde groups. These groups were also selected for the functionalization of the supports. The molecule chosen for the functionalization which provided the aldehyde-free groups was glutaraldehyde (GLUTA), a head-tail cross-linking molecule. In order to take advantage of the surface hydroxy groups which some supports could have, an alkoxysilane were employed in the functionalization as this linker was able to react with surface hydroxy groups of the support. 3-Aminopropyltriethoxysilane (APTS) was chosen as this alkoxysilane possesses an amine group which allowed the reaction with the aldehyde. In the case of Ti-alloys, instead of APTS, it was employed 3-aminepropyl phosphonic acid (3-APPA) as this was more reactive.

The activities carried out within the frame of WP3 allowed also to attain a step forward in extending the chemical strategies for the molecular surface functionalization of anatase TiO2 NP. The basic idea was to find an alternative to the exploitation of surface hydroxy groups as anchoring sites. The rationale was the limited amount of these groups on TiO2 anatase NP, resulting from the energy minimization of otherwise coordinative defective terminations and/or the dissociative adsorption of water molecules on surface facets with higher energy with respect to the {101} ones, which are the most stable, and typically the more abundant in usual TiO2 anatase NP. Conversely, {101} surfaces can strongly interact with phosphate/phosphate like groups, a behaviour typically observed when these nanoparticles, as such or in the form of coating of orthopaedic and dental implants, are used in cell-free tests or in-vitro and in-vivo experiments involving cells and/or tissues.

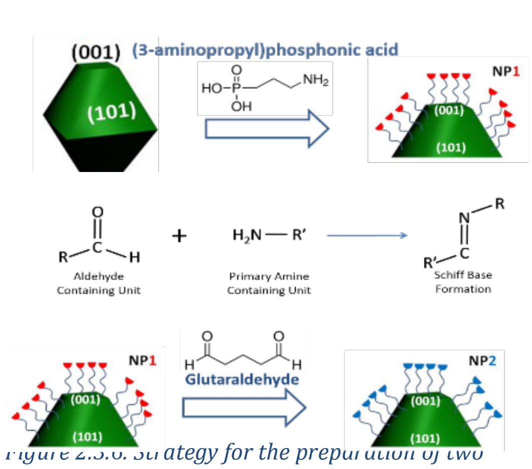


Figure 2.3.6. Strategy for the preparation of two complementary set of TiO2 NPs for film formation

On this basis, the 3-APPA functionalization with two types of TiO2 NP mostly terminated by {101}, namely TiO2 P25 and UT001 was successfully attained. The presence of the amino group intended as functional group exposed toward the exterior by {101} surfaces reacted with 3-APPA was functional to the subsequent reaction with GLUTA, used to covalently bound TiO2 NP to supports or to other TiO2 NPs, both treated in order to expose amino groups. A graphical summary of the overall chemical strategy pursued is displayed in the Figure 2.3..

The attainment of the scientific task constituted by the functionalization of TiO2 NP with 3-APPA required also the selection of proper characterization techniques, effective in probing the actual occurrence of the functionalization, in particular of the targeted type of surface terminations. This goal was successfully achieved too by using complementary technique. Among them, Auger Electron Spectroscopy (AES), combined with Transmission Electron Microscopy, as shown in figure 2.3.7, where TiO2 NP functionalised with 3-APPA, and then reacted with glutaraldehyde, is displayed.

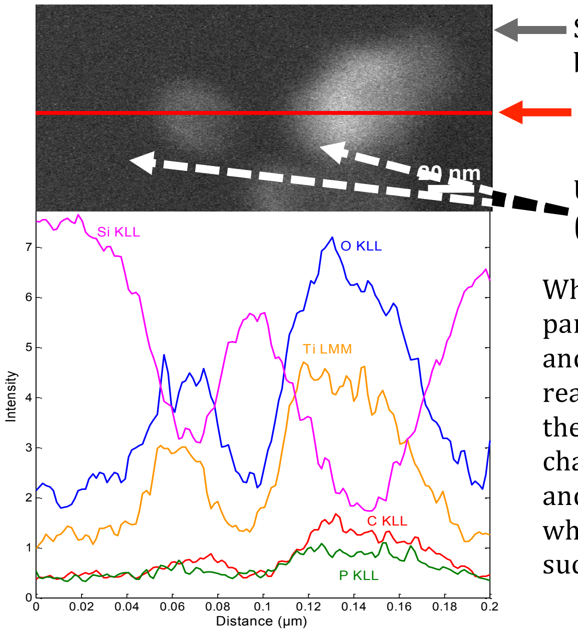


Figure 2.3.7. AES and TEM micrograph of the functionalizacion of TiO2 NPs

When the primary electron beam moves over the particles, the O and Ti signals (due to TiO2 NP) and C and P signals (due to 3-APPA) firstly increase, then reach a short plateau, and finally, decrease, whereas the Si signal coming from the Si wafer substrate, changes in a reciprocal manner. The variation of the C and P line scan intensities relates to the locations where the TiO2 NPs are present, monitors the successful functionalization with 3APPA.

Moreover, the anchoring of 3-APPA molecules to {101}surface terminations was proved by IR spectroscopy of CO adsorbed as a probe molecule on pristine and functionalised TiO2 NP: after anchoring 3-APPA molecules, the signal typical of CO in interaction with Ti^{4+} sites exposed by {101} appears significantly decreased in intensity.
Finally the layer-by-layer deposition was carried out with the functionalized NPs onto the functionalized supports. However, it was observed that the coverage of the support can attain almost to completeness, but only over limited areas, and the thickness of the multilayers of NPs appeared quite inhomogeneous. Conversely, PVD sputtering and screen-printing appeared methods suitable for coating supports using simpler technologies.

2.4 Characterization of individual TiO2 NPs and films resulting from their assembly/aggregation

The general aim of this WP was to improve existing methods for analysis of physico-chemical, mechanical, optical and electrochemical properties of TiO2 NPs and films so that these methods can be applied as reproducible measurement according to standard operation procedures (SOP). A number of 14 SOPs have been issued within WP4 reflecting the newest methodology of measurement of e. g. bipyramidal TiO2 NPs properties such as particle size and shape distribution by means of electron microscopy or elemental composition in-the-depth of TiO2 NP screen-printed layers loaded with ruthenium dye complex for solar cell applications. In most cases, significant methodical developments have been undertaken well beyond the state-of-the-art of the respective analytical methods for accurate measurement of the specific TiO2 NPs and layers fabricated in this project. Considerable part of the measurement procedures as developed under WP4 is either already published in scientific journals or submitted for publication or in preparation.
A special emphasis has been put on the metrological content of all WP4 SOPs with respect to a unitary structure including not only the exact description of the measurement procedure, but also the challenging aspects of method validation as well as the assessment of measurement uncertainties

associated to the result obtained. Furthermore, there where it was possible, modelling and simulation of the signals have been performed with the main purpose to estimate the accuracy of the measurement result. Three extensive reports related to modelling and simulation of X-ray spectra (with electron and X-rays as excitation probes) from TiO2 NPs and layers as well as on multiscale modelling using Simulink/Comsol for electrochemical properties and Matlab and Monte-Carlo for X-ray spectroscopy including the relationship to critical parameters (CP) and critical dimensions (CD) have been issued as corresponding WP4 deliverables.

An inherent part for ensuring the traceability of the results obtained after following the procedures recommended in the SOPs developed in WP4 is the exploitation of reference materials for calibration purposes. Due to the lack of suited certified reference materials (CRMs) in the field of nano-properties, potential candidates as CRMs resulted from WP1 (NPs as well as layers) with respect to e.g. dimensional (size and – in premiere - shape) properties have been identified and metrological pre-characterization necessary for further certification process (e.g. by BAM) carried out. An inter-laboratory comparison with well-shaped (bipyramidal) TiO2 NPs manufactured within SETNanoMetro has been organized within ISO/TC 229 Nanotechnologies with 18 participants such as Evonik, BASF, Kronos, FDA, NIOSH, PTB, NIST, AIST with the scope of including this study case into the ongoing standardization project ISO/WD 21363 Nanotechnologies -- Protocol for particle size distribution by transmission electron microscopy (TEM). Further, three WP4 SOPs have been already prepared to be submitted as working drafts to national standardization bodies (see later).

The most reliable analytical method applied for the measurement of size distribution of nanoparticles also of more complex shapes is the electron microscopy, TEM and scanning electron microscopy (SEM). The special challenge in this project was to measure a large amount of newly prepared batches of TiO2 NPs of variable shapes in a short time as characterization accompanying the fabrication process for further optimization of the controlled parameters via supporting predictive models from WP2. Hence, the further development of a new variant of TEM, namely transmission in an SEM (TSEM), could be advanced considerably for the dedicated application of measurement of size and shape distribution of bipyramidal shaped TiO2 NPs (Figure 2.4.1).

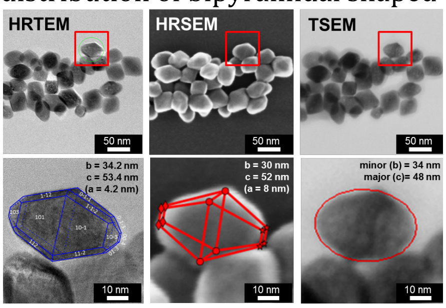


Figura 2.4.1: Electron microscopy micrographs of the same TiO2 NP imaged with different methods: TEM (left), high-resolution SEM (middle) and SEM in transmission mode, TSEM (right)

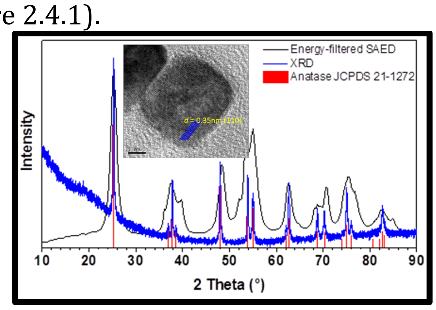


Figure 2.4.2: XRD pattern (blue) of a TiO2 NP powder sample together with JCPDS 21-1272 reference data of peak positions for TiO2 anatase (red) overlapped with an SAED spectrum (black) taken from an agglomeration of about 100 NPs over an area of about 30

The systematic dimensional characterization of the TiO2 NPs produced in SETNanoMetro has been complemented by the structural characterization carried out with different methods: X-ray diffraction (XRD), HR-TEM, selected area electron diffraction (SAED) at TEM and Raman Spectroscopy. Figure 2.4.2 shows the excellent agreement between the identification of pure anatase polymorph by XRD, SAED and HR-TEM for a specific batch of bipyramidal TiO2 NPs. A separate study on prepared mixtures of different TiO2 polymorphs (anatase, rutile and brookite) has demonstrated that Raman spectroscopy, a relative simple method sensitive to specific crystal vibration modes, yields reliable quantification of the individual TiO2 polymorphs. A corresponding SOP has been issued by WP4.

A special attention has been paid within a dedicated WP4 task to the accurate chemical analysis of the surface of TiO2 NPs as produced in SETNanoMetro. An Auger transition Ti LMV involving a valence level (V), as recorded by X-ray photoelectron spectroscopy (XPS), was demonstrated to provide templates for TiO2 phases (rutile vs anatase) and orientations that allow a quantitative analysis of TiO2 NPs. Additionally to the classical surface electron spectroscopies X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), which are techniques sensitive to changes of chemical bonding from a TiO2 polymorph to another, a special form of infrared (IR) spectroscopy (in controlled atmosphere) has completed the systematical characterization of TiO2 surface chemistry: by means of molecular probes, such as CO, which are sensitive to structure of adsorbing sites, detailed information not only on the individual TiO2 NPs surface sites but also on facets distribution, i.e. particles morphology, can be extracted from the corresponding IR spectra supported by density functional theory (DFT) calculations. Figure 2.4.3 illustrates correlation between the different CO absorption bands identified in IR spectra of different TiO2 nanoparticle materials (fabricated within SetNanoMetro and P25 from evonik) and different TiO2 surface structures.

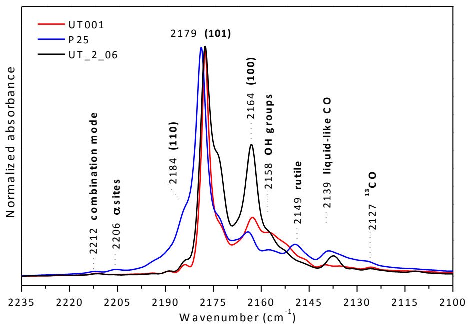


Figure 2.4.3: IR spectra for 4000 Pa of CO adsorbed at ca. 100 K on TiO2 NP samples outgassed at 873 K.

A multitude of TiO2 films have been manufactured and tested within SETNanoMetro with respect to their performances for the main three application fields (energy, environment and health). One basic film parameter is its film thickness. Depending of the TiO2 film type (sputtered by PVD or screen-printed) several sample preparation procedures from simple, quick and cheap, such as (i) scratch and cross-sectional SEM analysis of peeled-off fragments of layer or (ii) fracture of the layered sample followed by SEM cross-sectional analysis, to more complex and expensive, such as (iii) cross-sectional preparation of the layered sample by focus ion beam (FIB) and cross-sectional SEM analysis, or (iv) preparation of a TEM lamella and T(S)EM analysis) have been recommended in form of a comprehensive SOP, see Figure 2.4.4. The more complex procedures do not imply automatically a higher accuracy of the thickness measurement.

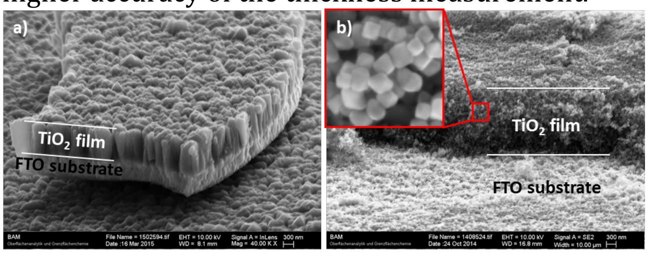


Figure 2.4.4: a) SEM micrograph of a physical vapor deposition (PVD) TiO2 film on transparent conductive oxide (TCO) glass substrate produced within SETNanoMetro and analyzed after scratching with a sharp blade, and b) fracture surface of a SETNanoMetro screen-printed TiO2 NP film on FTO glass substrates.

Other film parameters of crucial importance for the applications of the layered system as a product, but challenging to measure by traditional analytical techniques are porosity and the networking of the nanostructured TiO2 within the fabricated film, so that a quantitative evaluation of the inner surface of the porous TiO2 layer becomes possible. Figur 2.4.5 visualizes the 3-D reconstruction of the porous structure of unordered anatase NP coatings fabricated by screen-printing and analysed by FIB slicing and SEM imaging followed by data processing by appropriate binarization and segmentation – as described extensively in a dedicated SOP issued within WP4.

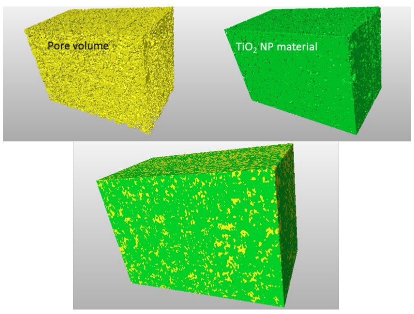


Figure 2.4.5: Separated volumes of pores (yellow) and material matrix (green) within a TiO2 porous layer.

Additionally to the results of the 3-D reconstruction of the porous TiO2 films by FIB slicing/SEM imaging, a new analytical technique, Transmission Kikuchi Diffraction (TKD) at SEM, could be applied successfully to extract quantitative information on orientation, size and shape of individual TiO2 NPs constituting the screen-printed layer.

The good accuracy of the results could be confirmed by independent AFM measurements of the same porous TiO2 films, see Figure 2.4.6. as well as by dimensional measurements with electron microscopy (TEM, SEM and TSEM) carried out on the TiO2 NP initial powder.

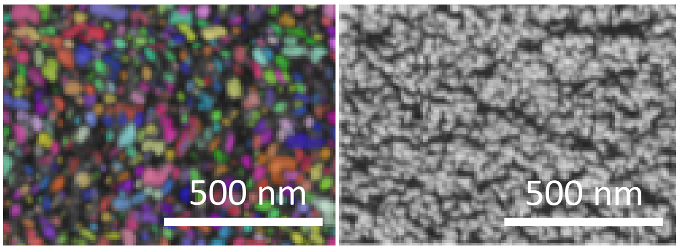


Figure 2.4.6: TKD orientation (inverse pole figure) map of a FIB lamella prepared from TiO2 NP layer (left), and atomic force microscope (AFM) image of the surface of the same layer.

The characterization of SETNanoMetro TiO2 NPs and their assemblies undertaken in WP4 is completed by detailed investigations of their mechanical and electrochemical properties.

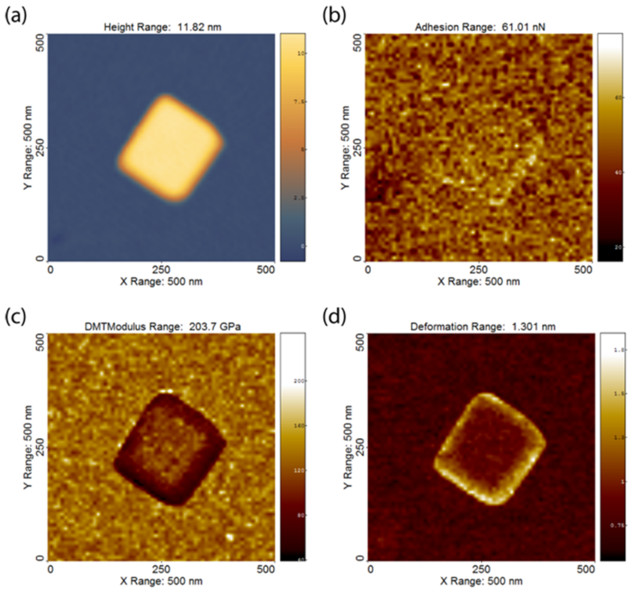


Figure 2.4.7 Quantitative AFM force mapping of a single TiO2 nanoplatelet lying on a Si substrate: a) height, b) adhesion, c) Young's modulus, d) deformation. Note the particle height of ~10.5 nm and deformation of ~0.9 nm

Figure 2.4.7 shows an example of analysis of mechanical properties at the nanometer scale for a single TiO2 nanoplatelet. Note the correlation between mechanical properties (adhesion, Young's modulus and deformation) to particle morphology.

As far as the electrochemical properties are concerned a corresponding task has been dedicated to measurements providing information on the photocatalytic behavior of TiO2 coatings, such as: band gap(see Figure 2.4.8), photocurrent / reaction kinetics, band bridging, and system capacitance (including surface, material and interfaces). Electrochemical measurements such as photo potential and photo current measurements, and impedance spectroscopy methods were used in combination with diffused reflection measurements. Using energy-loss electron spectroscopy (EELS), diffused reflection, and electrochemical methods, band gap at individual nano-particle level is compared with macro scale band gap (see Figure 2.4.9). In this way, it was possible to identify the spread in band gap of nano-powders based on the synthesis methods.

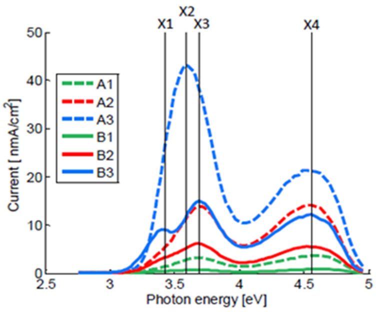


Figure 2.4.8: Photo-current measurements of various TiO2 coatings for 0.14 V (dashed lines) and 0.34 V (solid lines) vs. a standard hydrogen electrode: TiO2 on Al with intermediate layer of Ti (blue), TiO2 on 6 nm anodized Al_2O_3 layer (red), TiO2 on 22 nm anodized Al_2O_3 layer (green).

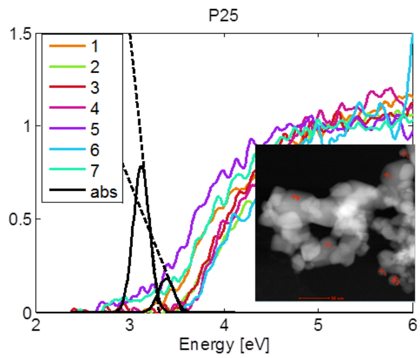
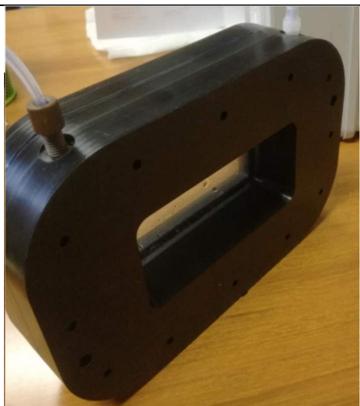


Figure 2.4.9: An example of comparison of macroscale band gap measurement using diffused reflection and individual particle level band gap using EELS. Sample P25 shows macro scale spread on band gap, which agrees with individual particle level band gap measured by EELS (on 7 locations/NPs).

2.5 Standardization rules for TiO2 NPs and films performances in photocatalysis

The main task of WP5 consisted of the development of traceable measurement methods of the photocatalytic activity of TiO2 crystals with focus on pre-normative recommendations and industrial application. The measurement methods encompassed macroscopic methods such as the standardized Methylene Blue decomposition, as well as newly constructed portable gas/solid and liquid/solid reactors. In addition, the photocatalytic activity has also been studied on the microscopic scale, down to the level of individual NPs. For this purpose, the existing measurement method of Scanning Kelvin Probe Microscopy (SKPM) has been made traceable to the work function property of metals. Several inter-laboratory comparisons have proven the various measurement methods to be in good agreement. Ultimately, in order to provide the same conditions for all measurement methods, and as a pre-normative approach for further standardization, prototypes of a new calibrated light source based on LED technology has been developed, built, and sent to the participants for best comparability of the measurement results.
The established measurement methods have been applied to TiO2 particles produced at an industrial scale, and the optimum design parameters for highest photocatalytic activity of the NP batches have been found. A reference standard for photocatalytic activity has been developed and is now commercialized by a consortium member. The work has led to 6 extensive major consortium reports on quantification, traceability and measurement uncertainty of photocatalytic activity at the nano- and micrometer scale, reference instrumentation and methods, as well as a comprehensive report on correlation and design rules. Outside the consortium, the work of WP5 has resulted in more than 5 peer reviewed publications, 2 under preparation, and more than 5 contributions to international conferences and workshops, and 5 prototypes/reference materials, out of which 4 are being made commercially available by the consortium.

Reference methods



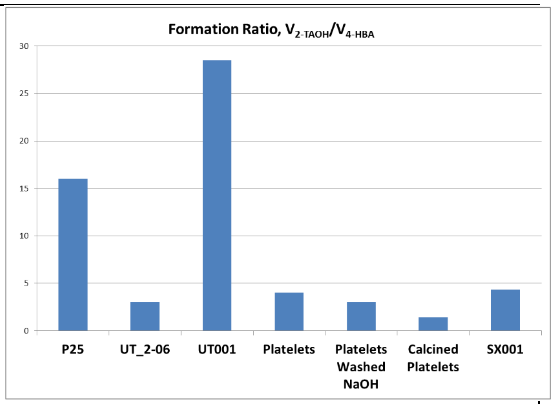


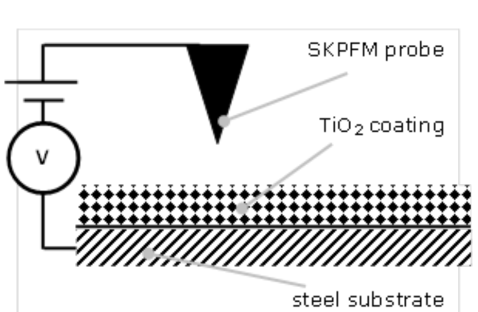
Photo of the gas/solid reactor (large) and the light source (inlet)	*Photo of the liquid/solid reactor*	*Performance measurement of various TiO2 materials as measured.*

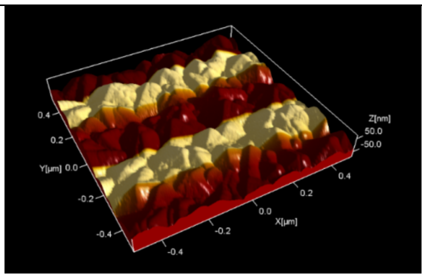
Figure 2.5.1 Gas/Solid and liquid solid reactors

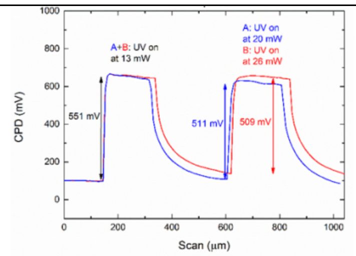
Gas/Solid and liquid solid reactors

For gas/solid and liquid/solid experiments portable miniphotoreactors have been developed (Figure 2.5.1). They are equipped with the reference LED source a set of various sensors (photoionization detector, electrochemical NO, CO and NO_2 sensors for gas/ solid, radiant power, pH, dissolved O_2 for the liquid/solid) for continuous monitoring substrate. The gas/solid set-up employs a continuously stirred tank reactor (CSTR) which allows extrapolation to infinite turbulence, thereby obtaining an evaluation of the photocatalytic activity that is independent to mass transfer. For liquid/solid experiments a flow through recirculated photo reactor has been developed that employs a fluidic optimized in order to give standard and reproducible conditions of illumination and flow. The photocatalytic activity is measured as substrate disappearance rate. An important requirement is also the speed of measurement and the possibility to carry out in-situ and in-line measurement. The miniphotoreactors have been especially designed to allow fast measurements. The main source of measurement uncertainty for both miniphotoreactors is the repeatability. Other contributions to the uncertainty are the concentration of the substrate, the flow, the radiant power of the light source. Noteworthy, the relative standard uncertainty is always lower than 5%.

SKPFM







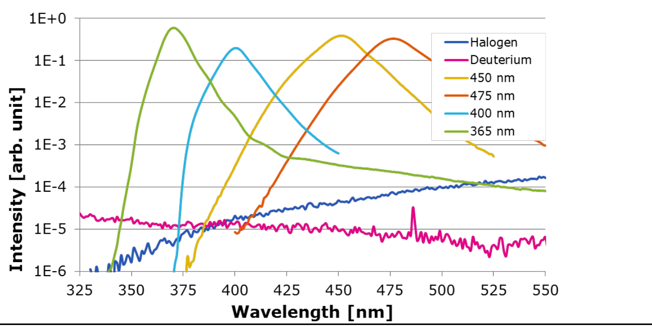
Schematic showing the principle of SKPM, where the CPD between the probing tip and the surface coating is measured.	*Micrometer topography scan of TiO2 NPs with colour overlay to show changes in CPD when UV source is switch on and off.*	*An example of measure CPD changes shown as line profiles.*

Figure 2.5.2 Scanning Kelvin Probe Measurement technique (SKPM)

Photocatalytic activity at the molecular level results in charge separation by the electron-hole generation. This change in surface potential can be measured using Scanning Kelvin Probe Measurement technique (SKPM) Figure 2.5.2, which responds to changes in the contact potential difference (CPD) between the nanometer sharp probing tip and the probed surface. SKPM images of sub-micrometer areas have been taken while exposing the same to standardized UV radiation and the CPD studied in detail. The relative standard measurement uncertainty on CPD changes caused by photocatalytic activity is in the order of 10%, dominated by the repeatability of the experiment.

Reference materials and instrumentation

Lights sources

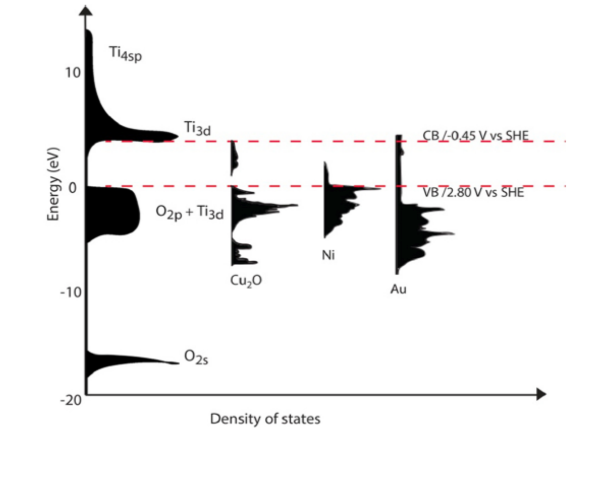


High efficient LEDs (peaks) outperform high-intensity light sources (flat lines) in spectral irradiance

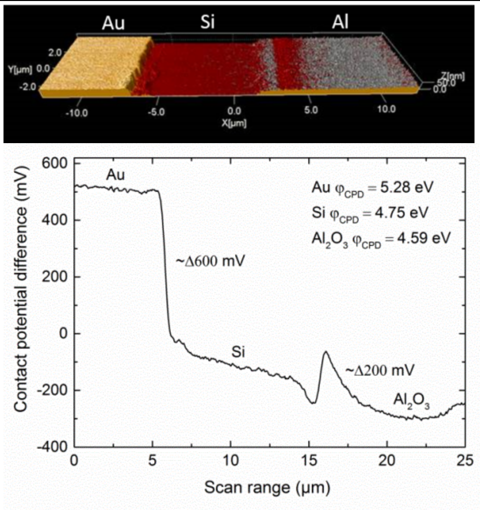
Figure 2.5.3 Lights spectra

A portable light source based on LEDs has been designed for multi-purpose applications in the project. Compared with a 20 W halogen and 25W deuterium lamp, the 1W LEDs outperform the broadband light source regarding the spectral power with a factor of 1 000 to 10 000. While being individually narrow banded, the combination of different wavelengths (Figure 2.5.3) together with digitally controlled drivers allow a sample irradiation at selectable and reproducible spectral regions. This allows maximum versatility, while at the same time providing robustness which minimizes shipping requirements during transportation among the partners. The spectral irradiances of the light source have been measured and are traceable to the SI-system of units. The expanded measurement uncertainty of the irradiance is approximated to 5%

Reference standard for traceability of photocatalytic activity at molecular level



Simplified band energy diagram of TiO2 in anatase form, Au, Ni and Cu(II) oxide

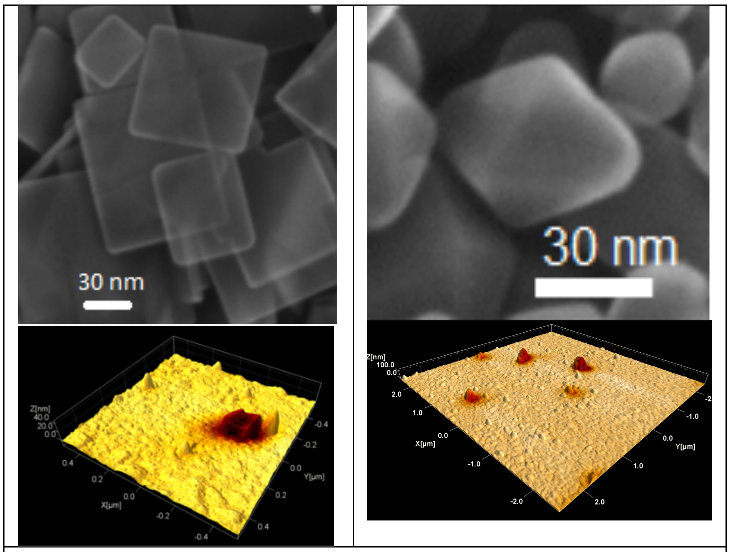


SKPMCPD image (top) of three metals (Au, Si, Al) and their work function differences (below)

Figure 2.5.4 Band energy and SKPMCPD

Traceability at the molecular level has been established to SKPM for the measurement of the photocatalytic activity during UV activation. The choice of using nanometer-flat gold coated substrates Au has been based on the extensive studies during the project (figure 2.5.4). Together with two other metals, the changes of TiO2 CPD during UV illumination can be related to the unaffected metal surface which established a potential scale using the work functions of the metals as a reference for calibration purposes.

Reference NPs materials

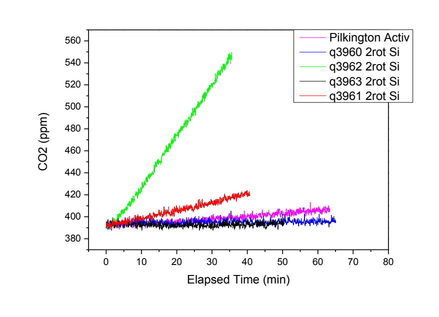


SEM images (top) of TiO2 nanoplatelets (left) and bipyramids (right), with the corresponding SKPM CPD images of the photocatalytic response (bottom) at level of individual NPs.

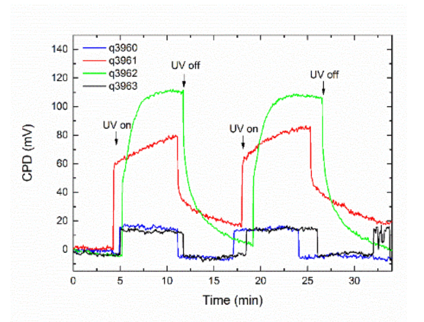
Two well-characterized candidate reference materials for the photo catalytic activity are chosen, TiO2 in bipyramidal form and nano-platelets. These different shapes and surfaces exposed, they encompass various aspects of the photocatalytic mechanism (OH radical like oxidation, direct hole transfer). Their photocatalytic activities were measured (Figure 2.5.5) reproducibly both on the molecular level and at a macroscopic scale, also within different NPs batches, ensuring the suitability of these materials as candidate reference materials for the photocatalytic activity. The production of the bipyramids has been scaled up to the industrial level, and thus led to the standard reference sample for photocatalytic activity, which is commercialized by project partner. The reference sample exhibits a change of CPD

Figure 2.5.5 TiO2 NPS characterization

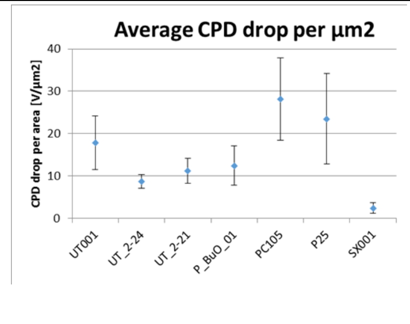
Correlating results on the molecular and macroscopic scale Optimum coating



PVD thin films: The photocatalytic activity measured as the degradation of acetone upon UV radiation (365 nm) on various samples.



PVD thin films: SKPFM measurement of the surface potential shift (CPD) upon UV radiation (broadband UV radiation).



Coatings of NPs: The total shift in CPD measured by SKPFM as a function of the area of the nanoparticle agglomerates that cause this shift.

Figure 2.5.6 inter-laboratory comparison (ILCs) on TiO2 PVD thin films

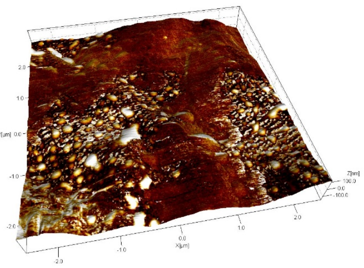
We have performed an inter-laboratory comparison (ILCs) (Figure 2.5.6) on TiO2 PVD thin films comprising of 4 different laboratories and measurement methods, as well as an ILC on TiO2 NP coatings down to individual NP level with 2 different methods. Furthermore, one ILC for the calibration task of coupling the macroscopic photocatalytic activity to the molecular level has been performed.

In the ILC on PVD thin films, the 4 utilized measurement methods were: 1) gas/solid acetone degradation, 2) standardized liquid/solid methylene blue, 3) liquid/solid OCP, and 4) SKPFM. The first three methods acquire the photocatalytic activity at the macroscopic scale, and the last on the molecular scale. Four TiO2 thin films deposited at different temperatures were analysed. All four measurement methods unanimously identified those thin films with the highest photocatalytic activity. Consequently, a correlation between measuring the photocatalytic activity at the macroscopic and the molecular level has been established, including an already standardized method.

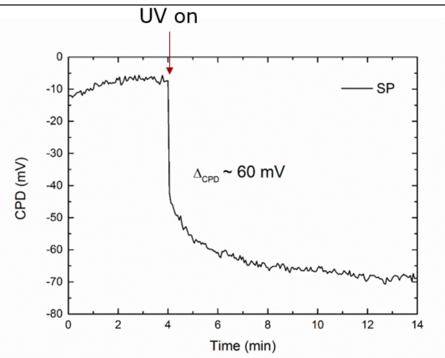
A correlation between the photocatalytic activity at the macroscopic and molecular level was also attained for coatings comprising of TiO2 NPs. Both the results from the gas/solid CSTR and from SKPFM indicated that the best photocatalytic performing NPs were UT001.

To establish traceability between the macroscopic and molecular level, TiO2 PVD thin films deposited on three different substrates (Au, Ni and Cu), where studied in an ILC between OCP and SKPFM [3]. Both techniques demonstrate that the substrate influence the achieved photocatalytic activity, and preferably the TiO2 thin film should be deposited onto Au due to an improved electron transfer when evaluated with SKPM.

Polymer embedded TiO2 particles



Topography image of TiO2 NPs embedded in a polymer pellet. The phase image is placed on top of the topography to highlight the particles in the surface of the pellet.



SKPFM on TiO2 NPs embedded in a pellet.

Figure 2 5.7 correlation between the macroscopic and the molecular photocatalytic

The established correlation between the macroscopic and the molecular photocatalytic performance (Figure 2.5.7) allowed for using SKPFM to determine the photocatalytic performance of TiO2 NPs embedded in polymer pellets. Above is displayed the topography showing embedded TiO2 NPs and the result from SKPFM.

2.6 Standardization rules for TiO2 NPs and films performance in DSSC

The photovoltaic performance of a Dye Sensitized Solar Cell (DSSC) relies on the characteristics of its photoanode, which plays a central role in converting light into electrical energy. A DSSC photoanode typically consists of a mesoporous oxide film on a transparent conducting glass substrate. Dye molecules that capture photons from light during device operation are attached to the surface of oxide film. Photoexcitation of the dye molecules leads to the injection of electrons into the oxide film. A key fabrication factor for high efficiency and reproducible DSSC is the dye loading of the film, which determines the quantity and the nature of the adsorbed dye molecules. The dye loading should be optimized so that the interfacial surface of the oxide film is completely covered with a monolayer of dye molecules.

Preparation of dye sensitized TiO2 films.

Staining conditions were optimized, in terms of solvent, concentrations and duration in order to reach the maximum dye loading of titania layer used to build laboratory high efficiency dye sensitized solar cell. These staining conditions were recorded in a Standard Operation Procedure (SOP) for dye loading (see D6.1) that defines the procedure for efficient and reproducible dye loading of the films.

State-of-the art devices were produced using nanocrystalline titanium oxide, having particle sizes around 18 nm as the support electrode (anode), on which a sensitizer (organic or ruthenium metal organic complex) was attached as monomolecular layer, thanks to its anchoring groups (carboxylic acids). The electrolyte contains the redox couple iodide/tri-iodide in an ionic liquids mixture, and acts as the charge carrying media to contact each dye molecule with the electric circuit.

***Characterization of the TiO2 films loaded with the dye sensitizer*.**

After application of the reproducible procedure of loading of the screen-printed TiO2 NP films with the Ru-complex dye 'N719' (Solaronix 535-Bis TBA) as described in D6.1, the distribution of elemental composition in-the-depth of the porous, µm-thick TiO2 layer has been investigated by energy-dispersive X-ray spectroscopy (EDX), Auger electron spectroscopy (AES) and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

The through-the-depth analysis by AES and ToF-SIMS is carried out in form of semi-quantitative analysis, which is well suited for the purpose of assessing in-depth homogeneity of the Ru-complex dye throughout the TiO2 layer; quantification of the in-depth elemental distributions through the ~7.5 µm TiO2 layer by means of the two analytical methods is not recommended due to large errors caused by various sources such as matrix effects, sample surface morphology effects (AES), or stability of the chemistry of the analysed surface during ion bombardment (SIMS).

The best AES results have been obtained on samples prepared for analysis after breaking them carefully and selecting a relative plane surface where an AES line scan could be collected. By taking into account the effect of surface morphology on the Auger electron intensities a relative homogeneous distribution of the dye sensitizer through the thickness of the porous TiO2 screen-printed layer can be concluded.

That the dye is homogenously distributed over the entire TiO2 film thickness was confirmed by ToF-SIMS analysis. Similarly to AES, the method is very sensitive to surface and the methods work in the depth-profiling mode (by alternating sputtering and analysis) for depth up to 100-200 nm. However, a dedicated ToF-SIMS measurement session (by individual overnight measurements) in the depth-profiling mode has been carried out on the same samples as in Fig. y. The result can be observed in Figure 2.6.1.

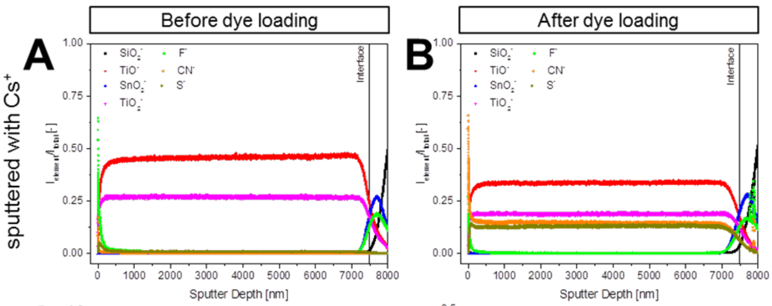


Figure 2.6.1. ToF-SIMS depth profiles of screen-printed TiO2-NP films on FTO-coated glass substrate before (A) and after dye loading (B).

No significant gradients along the thickness of the loaded TiO2 layer could be detected also by using EDX analysis on broken samples – similarly to the AES analysis. However, because the Ru X-ray signals were close to the limits of detection, mapping of three different depth areas has been carried out in order to collect X-rays with better signal-to-noise ratio.

N719 dye's concentration profile obtained on films by confocal Raman spectroscopy was described. Raman analyses were performed in order to consider the low thermal stability of the dye and the quantification of dye loading has been developed using a calibration model based on peak analysis. Due to its high spatial resolution, lower than 1 µm, Raman spectroscopy allows to analyse thin film sections. Raman analyses on film section were conducted in mapping mode. Using low laser power during Raman analysis has allowed accurate detection of analytes in restricted areas, and in Raman resonance condition the enhancement of dye signals. However, the main problem encountered was still the thermal degradation of N719 dye.

Characterization of the laboratory cells.

DSSC devices were produced using high stability state of the art electrolyte. The efficiency is correlated to the specific surface area and the dye loading of the titania layer. The reference material is still the best in terms of pure efficiency. The particles produced in WP1, UT001, show an efficiency that is really close from the reference material and a higher open circuit voltage in all the cases (see Table 1). It can be noted that this result is interesting as among all the titania nanoparticles that were tested in the past by SOLAR, few of them were able to compete with the reference (Ref-SX).

Cell No and type:	Isc (mA):	Voc (V):	Imp (mA):	Vmp (V):	Pmax (mW):	FF (%):	Rseries (Ω):	Rshunt (Ω):	Efficiency (%):
Average of SXP 12 samples	4.968	0.6936	4.344	0.498	2.164	62.85%	31.439	1738.3	6.01%
Average of UT001 11 samples	4.939	0.7083	4.319	0.520	2.247	64.23%	30.676	1366.0	6.24%

Tabel with Comparison of averages of main electric characteristics calculated from I-V curves

Efficiency is one of the criteria to evaluate to viability of a system but stability is critical in order to determine the usefulness of these nanoparticles in a potential device.
The stability of two types of DSSCs, made using the most promising titania nanoparticules, was investigated. Various ageing conditions were used like: (a) temperature: -27,5 °C; 50 °C; 70 °C, 85 °C (b) light soaking at 35°C and 70°C: light intensity 1000W/m², 400 nm UV filter in order avoid DSSC damage by UV (c) humidity: 80% (25°C)
On the basis of these investigations, it was found that:

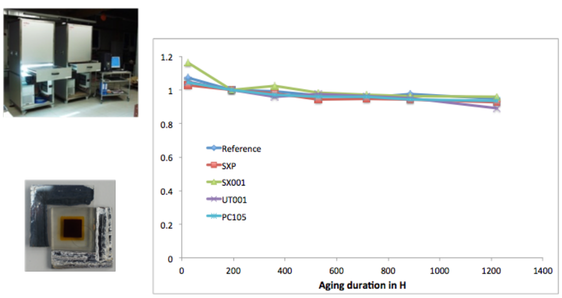


Figure 2.6.2. DSSCs ageing under constant llumination (65°C, 1sun AM 1.5G).

1. Temperature treatment at 50° C doesn't cause considerable change of DSSCs efficiency but treatment at 70° C causes a decrease of efficiency while heating at 85° C leads to a fast degradation of the cells.
2. Low temperature treatment (-27° C) doesn't influence the characteristics of DSSCs.
3. Light soaking (1000 W/cm², UV cut off) at 35°C doesn't influence efficiency of DSSC. Decrease of efficiency during light soaking treatment at 70°C is attributed only to the heating of samples during experiments.
4. Humidity (80 %) doesn't influence characteristics of DSSC
5. There is no influence of the nanoparticle type as the behavior is similar for all samples independently from the nature of the titania used in the device (Fig. 2.6.2). The devices were found to be stable under these conditions. The control of the device temperature seems critical to ensure a good stability under working condition.

2.7 Standardization rules for TiO2 NPs and films performances and toxicity in biomedical applications

Standard Operating Procedure for assessing the toxicity of various TiO2 nanoparticle coatings
We focus our work on test if TiO2 NPs that formed a surface coating on titanium/titanium alloy substrates would be present a low toxicity profile to cells relevant to tissue response to orthopaedic medical implants. The initial activities focussed on developing a Standard Operating Procedure for assessing the toxicity of various TiO2 nanoparticle coatings. This used two relevant cell lines, human osteoblast-like MG63 cells, and mouse macrophage RAW 264.7 cells, and utilised coated substrates that, when combined with an adhesive 8-chamber, allowed multiple independent cultures on the same substrate, which was designed to minimise sample-to-sample variability. Most of the studies were focussed on TiO2 NP coatings produced by magneton sputtering; these were initially on polished Ti6Al4V substrates but similar coatings were subsequently produced by first depositing a titanium substrate layer on glass slides, followed by deposition of the TiO2. The main observations were that all magnetron sputtered coatings, with different anatase: rutile ratios, exhibited negligible cell death, using the two different assays described in the SOP. Subsequent experiments with TiO2 NP coatings produced by screen printing of NPs and dip coating in a NP suspension showed similar results.

Together these results indicate that when NPs form a fixed coating they do not present a toxic response, relative to controls.

Another aspect that we investigate was the response of human mesenchymal stem cells (hMSCs) to various TiO2 NP coatings produced by magneton sputtering, to determine if these coatings supported osteogenic differentiation of the cells (medium supplemented with osteogenic supplements) and assess if any coatings appear to induce osteogenic differentiation (in the absence of osteogenic supplements in the medium). Initial activities developed an SOP that described the procedures for characterisation of the hMSCs use in such a study and the procedure for evaluating the cell response Results demonstrated that all TiO2 NP coatings supported the differentiation of the hMSCs to an osteogenic lineage, with positive upregulation of alkaline phosphatase (ALP) activity after 7 days and osteocalcin (OC) expression after 21-28 days culture in osteogenic medium (Deliverable 7.4); these studies used multiple donors, to eliminate the possibility of a donor-specific response. Although all coatings studied exhibited an increase in ALP activity when hMSCs were cultured with osteogenic supplements, coatings composed mostly of anatase produced the strongest results, whereas the coating composed mostly of rutile exhibited lower levels of ALP activity. These results were also supported by quantifying expression of COLIa1 and VEGF by hMSCs, which both showed higher expression for cells on anatase rich coatings, compared to rutile. The opposite was observed for TGF-β1 expression which showed a peak expression for hMSCs cultured on a rutile rich coating. No coatings appeared to induce osteogenic differentiation of hMSCs, with no significant differences between controls and coatings when no osteogenic medium was present.

The different TiO2 NP coatings produced by magneton sputtering that were characterised using a range of techniques to provide information of phase composition (XRD), surface roughness (AFM), surface morphology (SEM) and water contact angle. These properties were used to determine if any correlations existed with ALP activity, collagen (COLIa1) expression, VEGF and TGF-β1.

We observed some material property correlations, in particular the positive correlation between increasing anatase content with increasing surface roughness of the coatings. Additionally, we observed a strong negative correlation between increasing anatase content (and increasing surface roughness) and decreasing TGF-β1 expression. Anatase-rich coatings appeared to show stronger osteogenic differentiation of hMSCs, so expression of TGF-β1 may be suitable as a predictive marker of hMSC differentiation on such substrates. Such correlations ultimately must be validated through tissue responses, in this case bone deposition, in pre-clinical models.

Evaluation of toxicity in lung and intestinal cells

Since inhalation and ingestion are the two most important uptake routes for nanoparticles, the human lung epithelial cell line A549, the human colon epithelial cell line Caco-2 as well as the rat alveolar macrophage cell line NR8383 were chosen as three well-established test models. The initial activities focused on the developed of a SOP for toxicity profiling of the various TiO2 NPs. Evaluation of cell death, induction of markers of oxidative stress and inflammation were included since these are considered as the key biological pathways in nanotoxicology. Important aspects in the SOP include an accurate description of the preparation of the TiO2 suspensions, using a Cuphorn-sonication method, and additional measures to avoid assay read out artefacts in the toxicity testing. The SOP was then used to assess the effects of the three TiO2 commercial samples (SX001, P25, and PC001), alongside with samples designed and developed within the project. Amorphous silica NPs and a fine crystalline silica sample, were included in an assay specific manner, to allow for a hazard comparison with the TiO2 NPs. Cytotoxic cell death was determined with water-soluble tetrazolium (WST-1) assay. It was demonstrated that all tested TiO2 NPs had negligible toxicity in all cell lines, when compared to the SiO_2 NPs. As marker of oxidative stress induction, the mRNA expression of heme oxygenase-1 was determined by semi-quantitative real-time polymerase chain reaction (qRT-PCR). The TiO2 NPs caused mild oxidative stress only in the NR8383 macrophages. The inflammatory properties were evaluated by mRNA expression analyses of interleukin (IL)-1β, IL-6 and IL-8 (using qRT-PCR) and measurement of protein secretion of IL-1β and tumour necrosis factor-α (TNF-α) using enzyme-linked immunosorbent assay. Moreover, the activation of the NALP3 inflammasome cell signalling pathway activation was assessed in the NR8383 macrophages by evaluation of IL-1β secretion in lipopolysaccharide (LPS)-primed cells. Overall, the pro-inflammatory properties of the TiO2 NPs were minimal in comparison to the SiO_2 samples. The activation of the NALP3 inflammasome pathway emerged as a potentially discriminating effect for the "biological activity" of various TiO2.

The toxicity testing also included an in-depth evaluation of oxidative related DNA damaging effects of TiO2 NPs under varying illumination conditions. DNA damage was evaluated in the A549 cells by the comet assay, and revealed that specific TiO2 NPs could cause mild DNA strand breakage, but no oxidative DNA damage induction. Interestingly, however, after photocatalytic activation (using pre-illumination of the samples with UV-B) DNA damage and oxidation became more pronounced for a specific sample (p25). Subsequent intervention experiments with the antioxidant status modifying compounds BSO and NAC indicated that reactive oxygen species generated during UV-illumination could be responsible.

Another aspect that was investigated was the assessment of the oxidative potential of TiO2 NPs produced within the project by cell-free tests. The first part of the activities has been dedicated to the development of protocols based on Electron Paramagnetic Resonance (ESR) spectroscopy and UV/Vis spectrophotometry, ending with the definition of a Standard Operation Procedure. By using TiO2 samples (anatase, rutile and anatase/rutile mixed phase) of known photo-activity a set of protocols to assess the generation of Reactive Oxygen Species (hydroxyl radicals, superoxide anion radicals, singlet oxygen) and the reactivity toward lipids and nucleic acid moieties in a solution simulating the physiological pH and osmolarity were considered. Among the probes tested TEMPONE-H and DMPO in the presence of sodium formate appear the most suitable to predict the oxidative potential of the powders (Marucco A., Carella E. and Fenoglio I. RCS Advances 2015). These protocols were therefore chosen for the Standard Operation Procedure development.

In the second part, the SOP was used to assess the oxidative potential of four TiO2 samples, one developed in the project (UT001) and three commercial specimens (SX001, P25, PC001). The oxidative potential was evaluated in different illumination conditions, i.e. dark, indoor illumination, simulated sunlight and pre-illumination.

The results indicated that the intensity of illumination is an important parameter in vitro testing of photo-active semiconducting NMs. A significant photo-activation of the powders was in fact detected also in normal indoor light. Interestingly, pre-irradiation resulted in a small but significant generation of H_2O_2 for P25 and UT001 samples.

The effect of illumination on nanoparticles dispersion has been also evaluated by Dynamic Light Scattering (DLS). In this case, small effect of the light on the aggregates/agglomerates size distribution was observed in water. However, when proteins were present, a clear light-induced agglomeration was observed.

Overall, the results indicate that the control of illumination during toxicological testing is necessary to improve the inter-laboratory comparability of toxicological data.

Another aspect that was investigated is the hazard evaluation of the TiO2 NPs to contribute to safer-by-design strategies in the nanomaterial engineering field. This has been achieved by modelling of the relationship between the generated toxicological data and the physicochemical properties of the TiO2 NPs.

The availability of structure-activity relationships (SARs) is a mandatory pre-requisite for the design of safe chemicals. The principal component analysis (PCA) has been applied to find correlation among a set of physico-chemical properties, the oxidative potential, and the oxidative-stress related cellular response of a series of TiO2 nanomaterials prepared. The results of this analysis indicated a clear correlation among some toxicological outcomes, suggesting that a possible reduced number of parameters is sufficient to define the toxic response of the cells for TiO2 NPs. A correlation between the oxidative potential of the powders and their ability to induce Interleukin-1β release without or with LPS-priming activation was found. This indicates that the oxidative potential of TiO2 NPs is related to their ability to activate the NALP3 signalling pathway. Moreover, a relationship between the NP shape factor and NALP3 "activation" was found. Taken together, the chemical-physical variables analyzed seem to be a good set of variables to predict the toxicity (biological activity) with a soft model.

The toxicological data generated in the project with the various TiO2 NPs indicate that the hazard for this type of nanomaterial can be considered as low. Induction of inflammation and oxidative stress are considered as key "modes of action" that drive the adverse health effects of nanoparticles. The available literature reveals that, in comparison to other types of nanomaterials, the reactivity of TiO2 NPs towards cells is generally low (in studies that performed side-by-side comparison of various types of NPs). This was also specifically observed in the toxicity studies performed within this project. When tested on equal mass dose, the majority of effects of the TiO2 NPs, was lower than that of the amorphous SiO_2 NPs and, especially, in comparison to the fine crystalline SiO_2, which is a known toxic material. Notably, specific findings on DNA damage induction observed in this project align with a growing number of in vitro genotoxicity studies were small albeit statistically significant effects are shown for specific TiO2 NPs. In this regard, a major outcome from present WP is that the oxidative DNA-damaging properties of TiO2 NPs can be enhanced under illumination conditions. At which extent this is relevant for inhaled TiO2 NPs remains to be investigated, since lung tissue is not exposed to light. However, the observed findings can be of importance with regard to the specific handling of TiO2 NPs in toxicity testing protocols, as unintended, uncontrolled light exposures could result in false positive results (assay artefacts).

Finally, the toxicity data for the TiO2 NPs established within this WP should be viewed in relation to the applied treatment doses, since health risk is a function of exposure and hazard. This is also important regarding to the observed SARs for the TiO2. The findings from the PCA analyses indicate that it could be possible to lower the "biological reactivity" of this material "by design". This would further reduce the hazard of this relatively low toxic type of nanomaterial, and, under (non-controlled) high exposure situations, possible adverse health risks.

2.8 Standardization and scale-up of TiO2 nanoparticles at industrial level

WP8 was devoted to the scale-up of the TiO2 nanoparticles prepared in previous WPs, and in the study of the feasibility of their industrial scale-up and applications.

Scale-up of synthesis: sol-gel, hydrothermal and laser ablation.

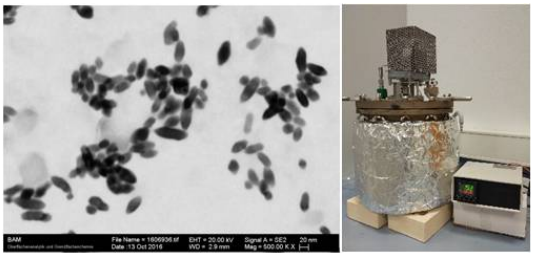
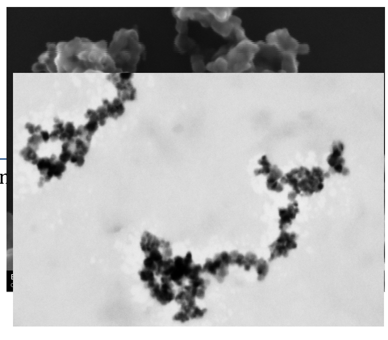


Figure 2.8.1: Hydrothermal reactor (left) and hydrothermal nanoparticles (right)

Laser ablation worked at very low concentration, in order to reach the nanoparticles with the expected quality assessed in previous WPs. Using the existent laser technology in UAB-MET, it was impossible to achieve kilograms scale, however different possibilities to achieve the process were explained and suitable equipment were proposed to achieve the scale-up.Hydrothermal technologies needed special reactors at high pressure (Figure 2. 8.1) to achieve the production. This methodology has gathered very good results in terms of controlling the morphology of the nanoparticles.In Setnanometro, AVANZARE has studied the preparation of hydrothermal nanoparticles in a 7 litres reactor. Different optimizations were proposed such as use of commercial precursors, low quality reagents, and even other techniques for purification of solid nanoparticles such as lyophilisation. Sensors for controlling these processes were not possible due to the pressure and temperature needed for the reactions.

Using sol-gel technologies, AVANZARE has prepared kilograms of the nanoparticles. AVANZARE has implemented different online monitoring system such as pH and temperature control, and also a surveillance camera in order to control the reaction in the long times needed.

Regarding high area nanoparticles by sol-gel technologies, (figure 2.8.2) the process was scaled-up in 400 times, reaching kilogram scale and aiming to obtain comparable results to laboratory scale.



AVANZARE has scaled-up the process, only introducing slight changes, such as an additional step of filtration and washing to eliminate some steps that create corrosion. Also, the recovery of the solvent by fractionated distillation will reduce the cost of the preparation of the product. The most time consuming step was the ageing of sol-gel that using high volumes, implies the use of longer times.
Low size nanoparticles by sol-gel technologies (Figure 2.8.2) have also scaled-up to kilograms scale in 300 times bigger than laboratory scale. AVANZARE has proposed a different point within the selected from TEKNIKER. In this way, the characteristics are very similar, but the required amount of reagents was optimized and the product was more likely to be scaled-up in a profitable way.

Recommendations of standardization procedures

Multiple informations was gathered along the project, in order to standardize procedures and create reference materials. Different protocols were proposed to characterize photocatalytic activity, based on all the techniques studied along the project to measure photocatalytic activity and characterize nanoparticles. The most interesting found along the project in liquid-solid systems were:

Figure 2.8.2: Low-size sol-gel

- Methylene-blue evolution using UV-VIS procedures
- HPLC coupled to the photoreactor system developed in the project
- Open circuit potential measurements using electrochemical equipment

Regarding gas-solid systems, the continuous stirred tank reactor developed in the project for measuring photocatalytic activity offered the best results. Two candidates for references were selected: hydrothermal nanoparticles for solid nanoparticles, and steel substrate coated with hydrothermal nanoparticles for coated surfaces. These rules were applied in the photodegradability of polymers such as varnishes or plastic parts. AVANZARE and TEKNIKER have prepared different samples loaded with nanoparticles such as varnishes, injected plastic parts or paintings (Figure 2.8.3). The samples were aged in QUV and were characterized using different techniques such as Raman spectroscopy, SEM-EDX or XRD. Using these techniques is possible to characterize the photodegradation capability of the nanoparticles, showing the following order: P25 > SOL-GEL HIGH AREA > SOL-GEL LOW SIZE > HYDROTHERMAL > PP VIRGIN.

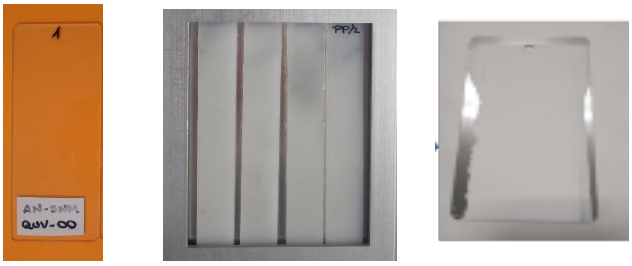


Figure 2.8.3: Glass coated with different varnishes (left and right), polymer injected part (middle)

AVANZARE has also prepared injected samples with nanoparticles and graphene in order to obtain conductive samples. In this case, it is possible to compare the photodegration activity by means of conductivity measurements. The obtained results were compared with the measurement of photocatalytic activity developed under the rules established in Setnanometro.

DFM has measured different polymer parts, and due to the low concentration in SKPFM, they have not shown photocatalytic activity. However using samples prepared by the direct deposition of the nanoparticles over steel surface is possible to see the same tendency in photocatalytic activity, although is worthy to note that high area sol-gel nanoparticles increase their activity in the highest concentration, obtaining better results than P25 nanoparticles

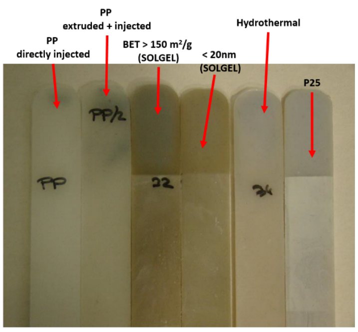


Figure 2.8.4: Plastic parts after aging

DSSC prototyping

The results collection obtained in task 6.5 has allowed to select the Dye Sensitized Solar Cell exhibiting the best functional performances and to be proposed as a standard, in terms of current, voltage and efficiency, with the fabrication of a prototype and the drafting of a protocol for its reproducible preparation.

W-type modules were investigated to build up a prototype, which consists in serially interconnected dye sensitized solar cells. Following the optimized and standardized procedures developed during the SETNanoMetro project, state of the art W-modules (10 x 10 cm, 65 cm^2 active area) were produced and fully characterized. The reproducibility of the performances was found to be good when comparing the modules to the test cells (7.86% for modules compared to 7.70% for lab cells) studied in WP6, which demonstrate the scalability of the process. The prototype stability was assessed as well, found to be good (Figure 2.8.6) and compatible with real outdoor use that is in agreement with TRL7 definition.

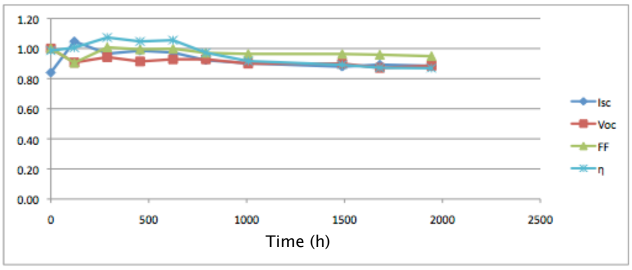


Figure 2.8.5 W-module prototype (left) and ageing curves (right) under constant illumination (1Sun AM1.5G, 65°C)

The reproducibility of the preparation for efficient DSSC modules was demonstrated on 10x10 cm scale according to the procedure that was developed during to project. Performance traceability was achieved by having the control on the whole characterization chain

3 Potential impact, main dissemination activities and exploitation of results

3.1 Impacts

Materials

The activities in WP1, in combination with WP2 and WP3, led to the formulation of design rules for the synthesis of size and shape controlled Anatase and Rutile nanoparticles, namely:

1 – bipiramidal TiO2 anatase NPs with low truncation (30-100 nm hydrodynamic diameter)
2 – elongated TiO2 anatase NPs with shape parameters from 2 to 6
3 – TiO2 anatase nanoplatelets with shape parameters from 0.15 to 0.30
4 – Prismatic rutile NPs with length from 150 to 1500 nm and shape parameters from 2.5 to 6
5 – Sol-gel TiO2 NPs with diameters < 20 nm
7 – high surface area sol gel TiO2 NPs
8 – spherical TiO2 NPs from LA

These particles can be exploited as shape and size standards in nanometrology, model materials for functional application (energy conversion in dye sensitized and perovskite solar cells, photocatalysis, ostheointegration of prostheses in the health sector, nanotoxicology) and standards for macroscopic functional properties in the sectors cited. These NPs will be synthesized by UNITO and commercialized by Solaronix. In Figure 3.1.1 is showed an example of the commercialized anatase nanoparticles.

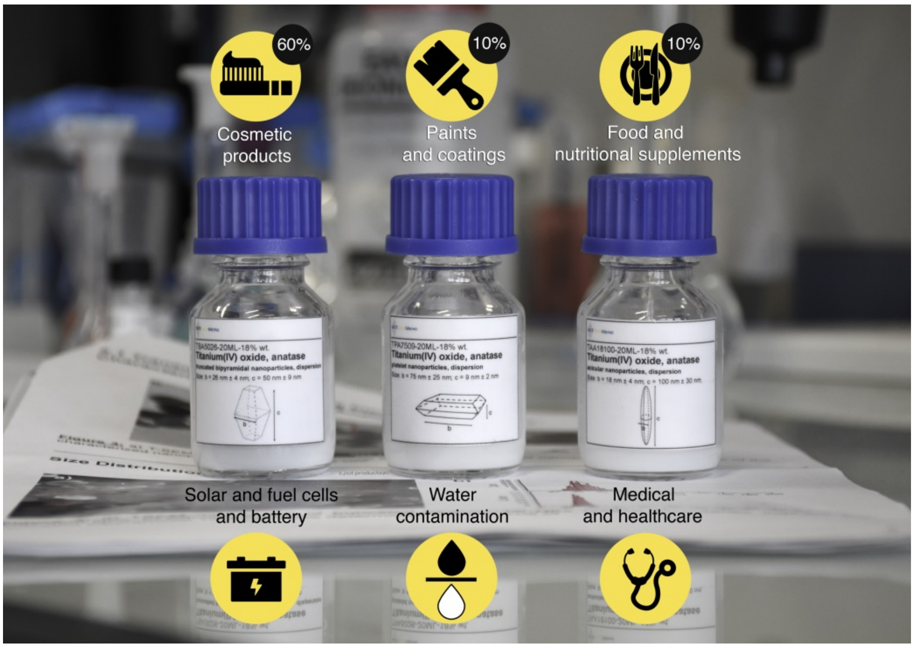


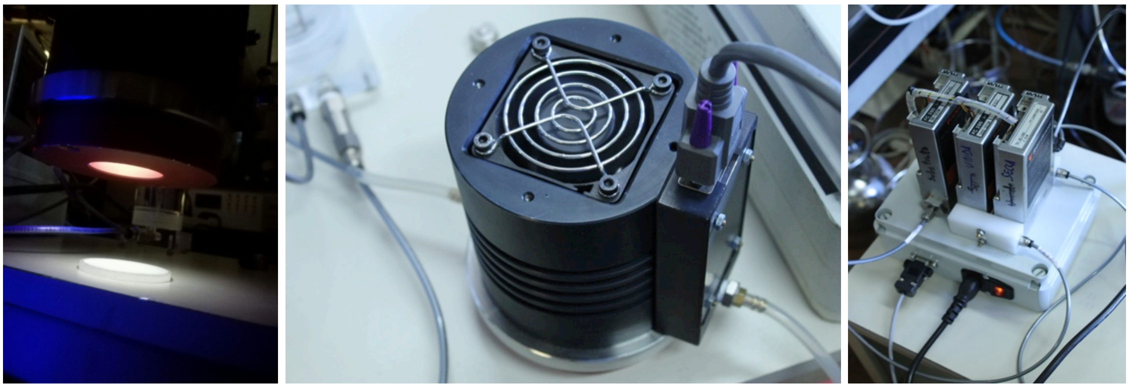
Figure 3.1.1. Size and shape controlled Anatase NPs produced and commercialized by SETNanoMetro partners.

Devices
Traceable and reproducible measurement of functional properties of nanoparticles assemblies and films is of paramount importance in order to establish correct correlation between properties at nanoscale and molecular level and the macroscopic functional properties.
In WP5 were developed two devices for fast, accurate and traceable measurement of photocatalytic activity of oxidic nanoparticles and films, both in gas-solid and liquid-solid regime.

Portable gas-solid photoreactor
The device developed has the following characteristics:

- Gas-Solid photoreactor for testing the abatement of gaseous pollutants on photocatalytic materials
- Turbulent reactor, extrapolation to infinite turbulence allows to measure intrinsic photocatalytic performances of the material, without problems of mass transfer
- Portable for in situ measurement, proprietary gasket assures very good seal on rough surfaces like concrete, possibility to control in situ the durability of materials
- Very Fast Response: 15 mL reactor chamber allows a complete measurement in minutes
- Option for different LED sources
- Control and regulation of Radiant Power with traceable calibration
- Option for different sensors and substrates (NO, Toluene, Acetaldehyde)
- Option for mounting 45 mm glass or metal disks for in lab testing of new materials and films
- Humidity and temperature control
- Automatic and manual operations with user friendly control software and a Standard Operating Procedure

The Beneficiary of this exploitable foreground is UNITO, and the Licence to equipment manufacturing was appointed to FONDERIA MESTIERI, Turin, Italy.
In Figure 3.1.2 is showed the running prototype of the portable gas-solid photoreactor and in Figure 3.1.3 and example of measurement.



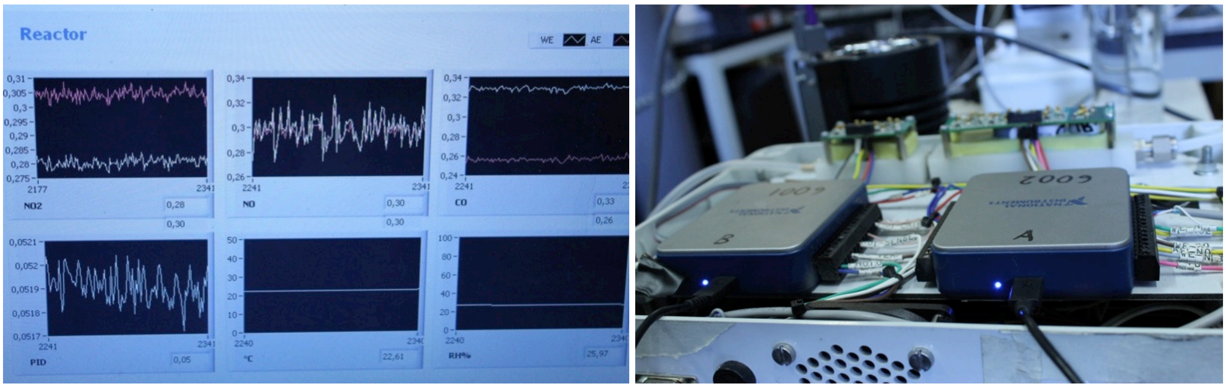


Figure 1.1.2. Gas Solid portable photoreactor, gas generating unit, control software user interface and control electronics.

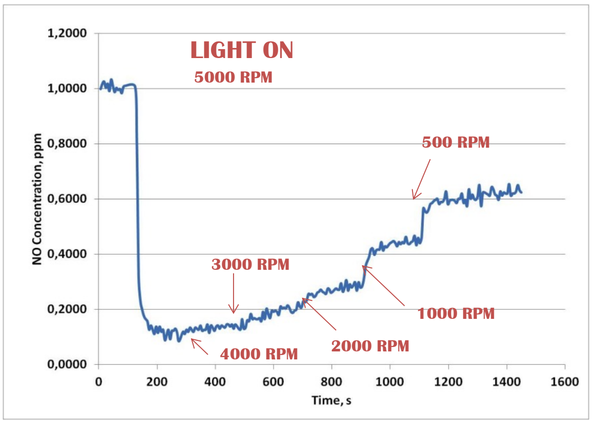


Figure 3.1.3. Example of a measurement of photocatalytic activity on SETNanoMetro NPs film (NO abatement).

Miniature photoreactor for fast, accurate and traceable measurement of photocatalytic activity in the liquid-solid regime

For the traceable measurent of photocatalytic activity of NPs suspensions and films was developed a flat recirculated miniphotoreactor. Particular care was devoted to the design of the fluidodynamic of the reactor in order to attain a homogeneous liquid flow in the illuminated region.

A standard operating procedure for its traceable use was developed, with a proper suite of substrates (melamine, phenol, terephthalic acid and formic acid). Also in this case there are option for different LED sources and control and regulation of Radiant Power with traceable calibration.

In figure 3.1.4 there is a sketch and a picture of the device. Figure 3.1.5 shows the particulars of the fluidic used to attain homogeneous flow in the irradiated area.

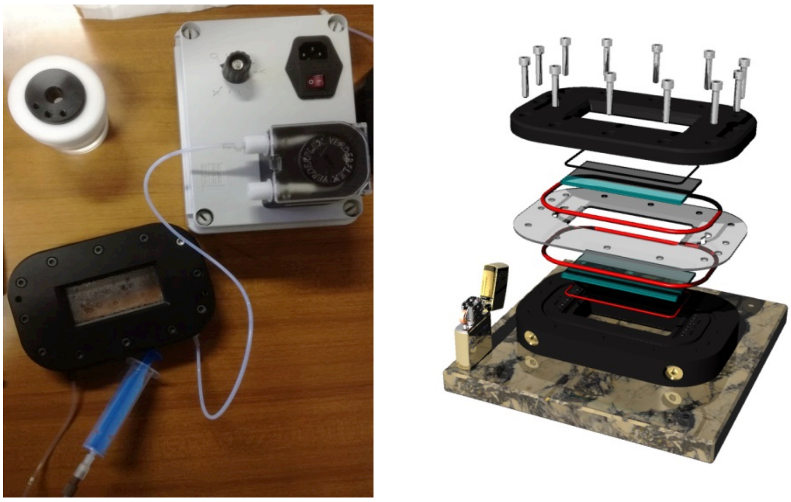


Figure 3.1.4. Picture and sketch of the flat recirculating miniphotoreactor for photoactivity testing in the liquid-solid regime. The photocatalyst can be in suspension or as a film deposited on the bottom window.

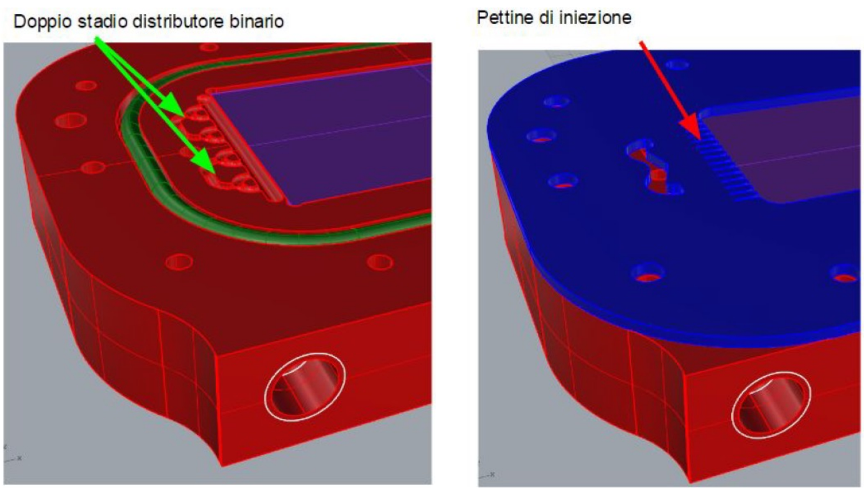


Figure 3.1.5. Particulars of the two stage binary flow distributor (left) and injection comb (right) to attain homogeneous flow.

The Beneficiary of this exploitable foreground is UNITO, and the Licence to equipment manufacturing was appointed to FONDERIA MESTIERI, Turin, Italy.

3.2 Dissemination and Exploitation

Dissemination and exploitation activities were covered by publishing articles in journals, contributing to national and international workshops and conferences, training of young scientists, performing of inter-laboratory comparisons and contributing to standardization. In addition, specific products were prepared for commercialization.

SETNanoMetro published 19 articles in scientific journals and additional 12 articles are under preparation. In addition, 34 oral presentations and 16 poster presentations were given at workshops and conferences. A publicly available website was created, where information about and created by the Consortium is available.

Clustering and training activities were also at the core of the dissemination tasks of SETNanoMetro. Even in the present global availability of information through the web, meetings offering to scientists the possibility to discuss, exchange ideas, debate, seed collaborations represent high added value actions. This target was pursued also by SETNanoMetro by organizing the international workshop “NANOSCIENCE meets METROLOGY: size and shape engineering of nanoparticles towards improved technologies for energy, environment and health”, held at the Ettore Majorana Foundation and Centre for Scientific Culture in Erice (Sicily, Italy) from 27th to 31st July 2015. The response of the European scientific community resulted in the presence of 54 participants, including the representative of 3 companies, Photocat A/S (Denmark) and the Italian branches of Thermofisher and Bruker (this last is a stakeholder of SETNanoMetro). The ensemble of participants gathered representatives from 8 European countries: Denmark, France, Germany, Italy, Netherlands, Switzerland, Spain and United Kingdom. In summary, the programme listed an introductory plenary lecture, 36 oral presentations, organized in 7 sessions, each opened by a keynote lecture, and in a poster sessions. The topics were dealing with emerging issues relevant for the European Research Area:

- need for characterization of the relationship between measurable key parameters through the nanoscale to the higher order scales
- interest toward the generation of reference information to test and optimise new design rules derived from length scale models;
- development of methods for measuring properties for which currently no methods exist, also ensuring the traceability, or at least the reproducibility, of existing methods;
- establish mechanisms to integrate new design rules to existing modelling techniques and apply these to industrially relevant materials and devices, delivering concrete results of industrial relevance

Programme and abstracts of the contributions are freely available at the Events page of the website of the project (www.setnanometro.eu), in the form of the digital copy of the Book of Abstract published with the ISBN code 978-88-97862-05-05.
The action in the field of training of young scientists was represented by the international summer school “NANOSCIENCE meets METROLOGY: synthesis, characterization, testing and applications of validated nanoparticles” held in Torino (Piedmont, Italy) on 4th-9th September 2016. The aim of the school was to offer to the young researchers international community the possibility to update and discuss on relevant topics of modern nanoscience and nanotechnology, augmented by their relationship with metrology. To this aim, two series of lectures were offered to participants. The first series was composed from wide-ranging lectures dealing with the results of the meeting of nanoscience with metrology in the fields of energy and environment, medicine and biology, upscale of applications from the lab to the industrial level. The second set was constituted by more specialized lectures on synthetic methods for validated nanoparticles (modeling the synthesis, controlling the morphology and guiding the aggregation), characterization methods for validated nanoparticles (electron microscopies, electronic and Vibrational spectroscopies, IR spectroscopy of surface probes), testing methods for validated nanoparticles (chemical and photochemical properties, biocompatibility and toxicology), applications of validated nanoparticles in catalysis, photocatalysis, medicine and biology. In total, the school was attended by 31 students, from Denmark, Finland, Ukraine, Spain, France, Germany, Italy, and from Brazil. Twenty-seven of them presented the results of their research projects in in the form of an extended abstracts, and among them nineteen accepted to act also as speaker in special sessions devoted to them, exploiting the opportunity to present their results to an international audience. In addition, these sessions were intended as a room for peer-to-peer discussion among students, with some inputs from more experienced researchers (the lecturers). Also, the ensemble of the abstracts of the lectures and of the students contributions are freely available at the website page indicated above (pdf of the Book of Abstract published with the ISBN code 978-88-87380-60-6)

Two inter-laboratory comparisons (ILCs) have been carried out within SETNanoMetro on most suited analytical methods for physico-chemical characterization of TiO2 nanoparticles (NPs) or their assemblies. From the list of fourteen deliverables generated by WP4 as standard operation procedures (SOPs) for the public domain on the measurement of physico-chemical parameters of titania (NPs or layers) the most suited procedure to be tested as an ILC was the measurement of TiO2 NP size and shape by electron microscopy. Two ILCs have been organized within JWG 2 "Measurement and characterization" of ISO/TC 229 "Nanotechnologies":

- Size and shape distribution of irregular primary titania crystallites by TEM,
  And
- Size and shape distributions of bipyramidal titania nanoparticles by TEM.

In the first ILC SETNanoMetro participated with two labs (TEM and TSEM, both situated at BAM), and the second ILC has been coordinated by BAM and has engaged 16 participants from 8 countries. The first ILC was included as a case study into the ongoing ISO/TC 229 standard ISO/WD 21363 "Nanotechnologies — Protocol for particle size distribution by transmission electron microscopy".
The second ILC organized by BAM with the SETNanoMetro samples UT001 followed - according to the recommendations of ISO/TC229/JWG2 group of experts – similar guidelines as the first ILC on titania. The same measurement and reporting protocol has been distributed by BAM to all participants together with the uniformly prepared TEM grids. Furthermore, clear descriptions regarding specimen handling, descriptors to be measured or calculated, instrumental parameters, tracing the particle shape (see Figure 3.2.1), number of particles to be measured, resolution of the captured image, analysis software, reporting data format and time scale have been written in the protocols.
An xls-template with the descriptors and instrumental parameters to be reported has been also distributed to all participants. The received data are being evaluated by BAM in a unitary way, according to the same general procedural steps used in the ILC #1. The first results will be presented at the next ISO/TC229 meeting (June 2017). Similarly to ILC #1 the final results of this ILC on bipyramidal TiO2 NPs are planned to be published. Further, the data will be exploited to initiate the procedure of certification (of size and shape distribution) of the reference material at BAM.

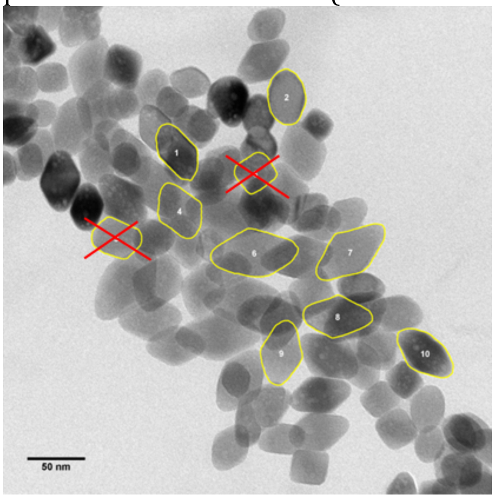


Figure 3.2.1 Example of data analysis (image processing) of the bipyramidal TiO2 NPs (UT001) containing manual particle shape tracing (see yellow contours) and fulfilling the criterion roundness >0.7 (see rejected NPs in red).

As given above, SETNanoMetro was in close connection to the standardization organizations. SETNanoMetro was supporting the development of ISO/TC 21363 "Nanotechnologies – Protocol for particle size distribution by transmission electron microscopy" by providing nanoparticles for an inter-laboratory comparison and participating in the comparison. SETNanoMetro was also supporting the development of ISO 19749 "Nanotechnologies – Measurements of particle size and shape distributions by scanning electron microscopy" by participating in the inter-laboratory comparison. In addition, SETNanoMetro was preparing two New Work Item Proposals for CEN/TC 352

"Nanotechnologies". A Project Liaison with CEN/TC 352 has already been established in May 2014. The two proposals "Structural bulk characterization of the TiO2 nanoparticles by IR and Raman spectroscopy" and "Characterization of the surface of TiO2 nanoparticles by FT-IR in controlled atmosphere" were announced to CEN/TC 352 during its last meeting on 23 March 2017 in Verneuil-en-Halette and will be presented in detail during the next CEN/TC 352 meeting in October 2017. The complete working drafts and application forms were prepared and sent to the Italian Standardization Organization UNI who will act as the official proposer of the proposals. Another proposal "3-D characterization of layers built from the deposition of nanoparticles using focused ion beam technique and scanning electron microscopy" was announced to ISO/TC 202 "Microbeam analysis" and will be presented in detail during the next ISO/TC 202 meeting in September 2017 in London. The complete working draft and application form was prepared and will be discussed on 4 July 2017 during the next mirror committee meeting of the German Standardization Organization DIN who will act as the official proposer of the proposal.

Last but not least SETNanoMetro developed some products which are prepared for commercialization. A specific bipyramidal titania will be purchased as certified nanoparticles, a second kind of TiO2 nanoparticles showing photocatalytic activity will also be purchased as a certified material. While these materials will be purchased in 1 g containers, a sol-gel derived TiO2 with photocatalytic activity developed by SETNanoMetro will be purchased in larger amounts. Another product derived from SETNanoMetro will be a Standard reference substrate for measurement of the photocatalytic activity of TiO2 films. And finally a photocatalytic reactor developed within SETNanoMetro can already be ordered.

4 Address of the project public website, relevant contact details.

SETNanoMetro website: www.setnanometro.eu

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DIN DEUTSCHES INSTITUT FUER NORMUNG E.V.	DIN	GERMANY	Michael.Schmitt@din.de
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FUNDACION TEKNIKER	IK4-TEKNIKER	SPAIN	miren.blanco@tekniker.es

5 Use and dissemination of foreground

5.1 Section A

5.1.1 Publications generated by SETNanoMetro

(published and in preparation)

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES

No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
1	Shape engineered TiO2 nanoparticles in Caenorhabditis elegans: a Raman imaging based approach to assist tissue-specific toxicological studies	INRIM	RSC Advances	6	Royal Society of Chemistry (RSC)	UK	2016	70501-70509	DOI: 10.1039/c6ra09686g	Yes	published
2	International Summer Workshop - NANOSCIENCE meets METROLOGY: "Size and shape engineering of nanoparticles towards improved technologies	INRIM + whole Consortium	-	-	Politeko Edizioni C.so Einaudi, 55 – 10129 Torino	Torino	2015	all	ISBN 978-88-97862-05-5	Yes	published

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES											
No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
	for energy, envirnoment and health"										
3	Comparing the photocatalytic activity of TiO2 at macro- and microscopic scales	DFM	Environmental Science and Pollution Research	(2016), published online	Springer	Online (open access)	2016	-	DOI 10.1007/s11356-016-7887-3	Yes	published
4	Mechanical properties of TiO2 nanocrystals	DFM	-	-	-	-	-	-	-	-	In preparation
5	Photocatalysis of thinfilms	DFM	-	-	-	-	-	-	-	-	In preparation
6	Characterisation of nanoparticles by means of high-resolution SEM/EDX in transmission mode	BAM	IOP Conf. Ser.: Mater. Sci. Eng.	109, 012006	IOP Publishing	Bristol, UK	2016	1-12	doi: http://dx.doi.org/10.1088/1757-899X/109/1/012006	Yes	published
7	In-depth structural and chemical characterization of	BAM	Surface and Interface Analysis	48	John Wiley & Sons, Ltd	Chichester, UK	2016	664–669	DOI: 10.1002/sia.5966	No	published

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES											
No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
	engineered TiO2 films										
8	New approach on quantification of porosity of thin films via electron-excited X-ray spectra	BAM	Analytical Chemistry	88	ACS Publications	Washington, DC	2016	7083-7090	doi: 10.1021/acs.analchem.6b00847	No	published
9	Size and shape distributions of nanocrystalline titania nodules in aggregated form: an interlaboratory comparison	BAM	Particle & Particle Systems Characterization	Not yet available	WILEY-VCH Verlag GmbH & Co. KGaA	Weinheim, Germany				No	Under revision
10	Ellipsometric Porosimetry on Pore-Controlled TiO2 layers	BAM	Applied Surface Science	Not yet available	Elsevier	Netherlands	2017		doi:10.1016/j.apsusc.2016.11.055	No	In press
11	Quick routine size and shape evaluation of bipyrmidal TiO2 nanoparticles by electron microscopy	BAM	Analytical Methods, ACS Nano?							-	under preparation
12	A new model for nano-TiO2 crystals birth and	RD (UNITO,	Crystal Growth &		American Chemical					-	submitted

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES											
No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
	growth in hydrothermal process using oriented attachment approach	BAM)	Design		Society						
13	Design Rules for the Hydrothermal Synthesis of Shape and Size Controlled Anatase NPs	UNITO (RD, BAM, INRIM)								-	in preparation
14	TiO2 nanoparticles generation by femtosecond laser ablation in water	MET , UNITO, BAM	-	-	-	-	2017	-	-	-	In preparation
15	Quantification of Anatase and Rutile in TiO2 Nanoparticles synthesized by Laser Ablation	INRIM, MET	-	-	-	-	2016	-	-	-	In preparation
16	Thin Film Nanocrystalline TiO2 Electrodes: Dependence of Flat Band Potential on pH and Anion Adsorption	UNITO	Journal of Nanoscience and Nanotechnology	Vol. 15			2015	3348–3358,		-	published

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES

No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
17	A comparative study on the efficacy of different probes to predict the photo-activity of nano-titanium dioxide toward biomolecules	UNITO	RSC Advances	2015, 5			2015	89559 - 89568	DOI: 10.1039/c5ra14303a	Yes	published
18	A proof of the direct hole transfer in photocatalysis: the case of melamineA comparative study on the efficacy of different probes to predict the photo-activity of nano-titanium dioxide toward biomolecules	UNITO	Applied Catalysis A: General				2015		doi:10.1016/j.apcata.2015.11.012	Yes	published
19	On the simple complexity of carbon monoxide on oxide surfaces: Facet specific donotation and backdonotation effects revealed on TiO2 anatase nanoparticles	UNITO	ChemPhysChem	17	Wiley		2016	1956-1960	doi: 10.1002/cphc.201600284	Yes	published

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES

No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
20	A surface science approach to TiO2 P25 photocatalysis: an in situ FTIR study of phenol photodegradation at controlled water coverages from sub-monolayer to multilayer	UNITO	Appl. Catal. B: Environmental							Yes	published
21	Influence of Agglomeration and Aggregation on the Photocatalytic Activity of TiO2 Nanoparticles	UNITO	Appl. Catal. B: Environmental		Elsevier		2017		Doi: 10.1016/j.apcatb.2017.05.046	No	Accepted
22	International Summer School - NANOSCIENCE meets METROLOGY: "Synthesis, Characterization, Testing and Applications of Validated Nanoparticles"	UNITO + whole Consortium	-	-	Politeko Edizioni C.so Einaudi, 55 – 10129 Torino	Torino	2016	all	ISBN 978-88-87380-60-6	Yes	published

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES											
No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
23	Photoemission Fingerprints for StructuralIdentification of Titanium Dioxide Surfaces.	UPMC	Journal of Physical Chemistry Letters	2016, 7	ACS		2016	3223-3228	DOI: 10.1021/acs.jpclett.6b01301	-	Published
24	Investigation of DC magnetron-sputtered TiO2 coatings: Effect of coating thickness, structure, and morphology on photocatalyticactivity	DTU	Applied Surface Science	313	ELSEVIER	North-Holland	2014	677–686		-	published
25	Interfacial microstructure and photocatalytic activity of magnetron sputtered TiO2 on conducting metal substrates	DTU	ACS Appl. Mater. Interfaces	6 (24)	American Chemical Society		2014	22224–22234	DOI: 10.1021/am5059298	-	published
26	Effect of the interfacial oxide thickness on the photocatalytic activity of magnetron sputtered TiO2 coatings on aluminum substrate	DTU	Phys. Status Solidi A,				2015	1–11	DOI 10.1002/pssa.201532238	-	published

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES											
No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
27	Photocatalytic properties of TiO2 nano particles from macro to nanoscale	DTU					2017			-	under prepara tion
28	Photocatalytic analysis of sol gel synthesized titanium dioxide nanoparticles with optimized size and surface area	DTU					2017			-	Under prepara tion
29	Analysis of photocatalytic properties of DC magnetron sputtered TiO2 coatings deposited at different temperatures	DTU					2017			-	Under Prepara tion
30	Nanotoxicological assessment of shape-engineered titanium dioxide nanoparticles	IUF	N aunyn-Schmiedeb erg´s Arch Pharmacol :S70	388 (Suppl 1)	Springer	Germany	2015	S70	DOI 10.1007/s0 0210-015-1087-4	Yes	publish ed
31	Toxic and inflammatory effects of	IUF	Naunyn-Schmiedeb	389 (Suppl 1)	Springer	Germany	2016	S54	DOI: 10.1007/s00	No	publishe d

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES											
No.	Title	Main author	Title of the periodical or series	Number, date or frequency	Publisher	Place of public-cation	Year of publi-cation	Relevant pages	Permanent identifiers (if available)	Is/Will open access be provided?	Status
	shape-engineered titanium dioxide nanoparticles in NR8383 rat alveolar macrophages		erg's Arch Pharmacol						210-016-1213-y		

5.1.2 List of dissemination activities

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
1	Presentation	INRIM	SETNanoMetro: Shape-Engineered TiO2 Nanoparticles for Metrology of Functional Properties	26 – 28 November 2014	NanotechItaly 2014, Venice, Italy	Scientific Community, Industry	50	EU	Presented
2	Presentation	INRIM	SETNanoMetro: Shape-Engineered TiO2 Nanoparticles for Metrology of Functional Properties	26 November 2015	CEN TC 352, Warsaw, Poland	Scientific Community, Industry	25	EU	Presented
3	Meeting	INRIM	Collaboration	28 September 2015	Mario Negri Milan Italy	Scientific Community,	5	Italy	Presented
4	Invited presentation	INRIM	SETNanoMetro: Shape-Engineered TiO2 Nanoparticles for Metrology of Functional Properties	6-9 September 2015	FRANCO-ITALIAN WORKSHOP ON NANOSCIENCE ISOLA DI PORQUEROLLES-FRANCIA	Scientific Community,	50	EU	Presented
5	Presentation	INRIM	Bio-accumulation of TiO2 nanoparticles in	27 – 31 July 2015	International Summer Workshop	Scientific Community,	54	EU	Presented

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
			caenorhabdities elegans an in vivo model for toxicity analysis		NANOSCIENCE meets METROLOGY, Erice, Italy				
6	Presentation	INRIM	Shape engineered TiO2 nanoparticles in Caenorhabditis elegans: a Raman imaging based approach to assist tissue-specific toxicological studies	14-19 August 2016	International conference on Raman spectroscopy ICORS	Scientific Community, Industry	100	Brazil	Presente d
7	Presentation	INRIM	Recognition and Quantification of Anatase, Rutile and Brookite in Binary Mixtures: a Raman Spectroscopy and Chemometric Study	14-19 August 2016	International conference on Raman spectroscopy ICORS	Scientific Community, Industry	100	Brazil	Presente d
8	Conference	DFM	Towards standardization and design rules for photocatalytic TiO2	June 13-17 2016	Strasbourg	Scientific community	500	Europe	Finished

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
9	Workshop	DFM	Funktionaliserede overflader – Bekæmpelse af biofilm ved fotokatalyse i nanocoatings	1 March 2016	Copenhagen	Scientific community, Industry	11	Denmark	Finished
10	Presentation	BAM	Charakterisierung von TiO2-Nanopartikeln mit kontrollierter Form mittels Rasterelektronenmikro skopie (SEM und TSEM)	9 July 2014	DIN-Workshop Methoden zur Präparation von Partikeln auf Substraten und Strategien zur Messung mit Elektronenmikrosk opie (SEM) und Rasterkraftmikrosk opie (AFM), Berlin, Germany	Scientific Community, Industry	34	Germany	presente d
11	Poster	BAM	Imaging of shape-engineered TiO2 Nanoparticles by high-resolution SEM/EDX	3 – 7 May 2015	EMAS 2015 (European Microbeam Analysis Society 2015), Portoroz, Slovenia	Scientific, Industry	200	Europe, USA, Japan, Canada, Russia, China,...	presente d
12	Presentation	BAM	Characterization of nanoparticles by means high-resolution	3 – 7 May 2015	EMAS 2015 (European Microbeam	Scientific, Industry	200	Europe, USA, Japan, Canada,	presente d

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
			SEM/EDX		Analysis Society 2015), Portoroz, Slovenia			Russia, China,…	
13	Poster	BAM	Porosity of highly porous thin films by X-rays at SEM	3 – 7 May 2015	EMAS 2015 (European Microbeam Analysis Society 2015), Portoroz, Slovenia	Scientific, Industry	200	Europe, USA, Japan, Canada, Russia, China,…	presented
14	Presentation	BAM	Morphological and chemical characterization of engineered TiO2 NPs and assembled films - an excerpt from the EC/FP7 project SETNanoMetro	17 April 2015	CCQM - Surface and Micro/Nano Analysis Working Group (SAWG) Meeting for 2015, Paris, France	National Metrological Institutes	25	Europe, Japan, USA, Russia, Brasil, Turkey, Korea	presented
15	Poster	BAM	Thin Film Porosity Determined by X-Rays at SEM	2 – 6 August 2015	Microscopy & Microanalysis 2015 Congress, Portland, USA	Scientific, industry	2200	USA, Europe, Japan, Canada,…	presented
16	Poster	BAM	Accurate Shape and Size Determination of Engineered NPs by Electron Microscopy (SEM, T-SEM, TEM,	6 – 11 September 2015	Microscopy Congress MC2015, Göttingen, Germany	Scientific, industry	1500	Europe, USA, Japan, Canada,…	presented

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
			SAED)						
17	Poster	BAM	SEM/EDX for the Determination of Thin Film Porosity: Application to mesoporous TiO2 layers	6 – 11 September 2015	Microscopy Congress MC2015, Göttingen, Germany	Scientific, industry	1500	Europe, USA, Japan, Canada,...	presente d
18	Presentation + Poster	BAM	Characterization of shape-engeneered TiO2 nanoparticles by SEM/TSEM	15/16 September 2015	Workshop on Analytical Transmission Scanning Electron Microscopy, Boulder, USA	Scientific, industry	35	USA, Europe, Japan, Canada,...	presente d
19	Presentation	BAM	Thin Film Porosity Determined by X-Rays at SEM: Application to mesoporous	14/15 October 2015	Bruker Workshop Days for Microanalysis, Berlin, Germany	Industry, Scientific	100	Germany	presente d
29	Poster	BAM	Comprehensive morphological and chemical characterization of thin engineered TiO2 films	28 September – 1 October 2015	16th European Conference on Applications of Surface and Interface Analysis (ECASIA 15), Granada, Spain	Scientific, Industry	300	Europe, USA, Japan, Canada,...	presente d
21	Presentation	BAM	Inter-laboratory Comparison (ILC) on	10-12 May 2016	ISO/TC229 (Nanotechnologies)	National standardisati	50	37 participatin	Presente d + ILC

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
			Shape of bipyramidal TiO2 NPs by TEM		/JWG2 (Measurement and characterization)	on bodies + industry + academia		g countries	accepted to be started within TC229/JWG2
22	Presentation	BAM	Inter-laboratory Comparison (ILC) on Size and Shape Distribution of bipyramidal TiO2 NPs by TEM	7-10 November 2016	ISO/TC229 (Nanotechnologies) / JWG2 (Measurement and characterization)	National standardisation bodies + industry + academia	50	37 participating countries	Progress of ILC presented and critically discussed.
23	Oral presentation	RD	Modelling the Discontinuous TiO2 Anatase Crystals'Growth in Hydrothermal Synthesys	27th July 2015	International Summer Workshop NANOSCIENCE meetsMETROLOGY, Erice, Italy	Scientific Community Industry	40	EU countries	presented
24	Oral presentation (by TEKNIKER)	TEKNIKER (RD, BAM)	Synthesis of TiO2 Nanoparticles with Controlled Characteristics by Sol-Gel Technology	27th July 2015	International Summer Workshop NANOSCIENCE meetsMETROLOGY, Erice, Italy	Scientific Community Industry	40	EU countries	presented

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
25	Presentation	AVANZARE	Casos prácticos de participación en el VII programa marco. Itinerario 'Europa mas cerca'	10.2.2014	Infoday HORIZON 2020, Logroño, Spain	Industrial	>50	Spain	presented
26	Presentation	AVANZARE	Development of multifunctional composites based on n-TiO2 and graphene with automotive applications.	4-9th September 2016	Nanoscience meets Metrology. International Summer School. Torino. Italy.	Academic	40	UE countries	presented
27	Poster	MET	Study of TiO2 nanoparticles crystalline phase by pulsed laser ablation in aqueous media.	27 July – 31 July 2015	"NANOSCIENCE meets METROLOGY", Erice, Italy	Scientific community, students.	54	Italy, France, Germany, Spain, Denmark, Lithuania, Netherlands, Romania, Switzerland, Great Britain	presented
28	Poster	MET	Preparation of TiO2 nanoparticles by pulsed laser ablation in surfactant solution.	27 July – 31 July 2015	"NANOSCIENCE meets METROLOGY", Erice, Italy.	Scietific community, students	54	Italy, France, Germany, Spain,	presented

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
								Denmark, Lithuania, Netherlands, Romania, Switzerland, Great Britain	
29	Meeting	MET	Collaboration	3 May 2016	Laser Research Center, Vilnius, Lithuania	Scientific Community	5	Lithuania	presented
30		UNITO	Effects of shape controllers on the surface structure of engineered nanoparticles: investigations with molecular resolution	14 – 18 September 2015	1st European Conference on Physical and Theoretical Chemistry, Catania, Italy				
31	Poster Presentation	UPMC	Oxide nanocrystallites with facets of controlled orientation	27th July 2015	International Summer Workshop NANOSCIENCE meetsMETROLOGY, Erice, Italy	Scientific Community Industry	40	EU countries	presented
32	Invited Conference	UPMC	Flexible oxidesurfaces	27th July 2015	International Summer Workshop NANOSCIENCE meetsMETROLOGY,	Scientific Community Industry	40	EU countries	presented

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
					Erice, Italy				
33	Oral presentation	UPMC	Surface identification of titania polymorphs by photoemission spectroscopy	4th july 2016	6th International Conferenceon NANOstructuresan d nanomaterialsSElf-Assembly, Catania, Italy	Scientific Community Industry	100	EU countries	Presente d
34	Oral presentation	UPMC	Identification of surface structures of titania nanoparticles by photoemission spectroscopy	28th august 2016	32th conference of surface science (ECOSS), Grenoble, France	Scientific Community Industry	>1000	EU countries	Presente d
35	Oral Presentation	UPMC	Identification of surface orientation of titania nanoparticles by photoemission spectroscopy	9th-14th October 2016	13th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSIN)	Scientific Community Industry	300	Europe, USA, Japan, Canada,…	Presente d
36	Invited Conference	UPMC	Defective oxide surfaces	24th May 2016	Elspec 2016 (Electron Spectroscopy), Meudon, France	Scientific Community Industry	200	France, Belgium, Algeria, Tunisia, Morocco,	presente d

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
								UK, Portugal, Italy, Germany, Turkey, Austria	
37	Oral presentation	UPMC	Electron spectroscopy for the nanometer scale	27 July – 31 July 2015	"NANOSCIENCE meets METROLOGY", Erice, Italy.	Scientific community, students	54	Italy, France, Germany, Spain, Denmark, Lithuania, Netherlands, Romania, Switzerland, Great Britain	presented
38	Oral presentation	UNIABDN	Chick models for in vivo screening of nano-sized TiO2 particles and other biomaterial nanoparticles	27th July 2015	International Summer Workshop NANOSCIENCE meetsMETROLOGY, Erice, Italy	Scientific Community, Industry	40	EU countries	presented
39	Oral presentation	UNIABDN	Biocompatibility of DC magnetron-sputtered TiO2 coatings with nano-scale morphology	18th-21st October 2016	Bioceramics 28 - The 28th Symposium & Annual Meeting of	Scientific Community Industry	150	Europe, Japan, USA, Canada, Brazil,	presented

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
			on Ti6Al4V and glass substrates		the International Society for Ceramics in Medicine, Charlotte, North Carolina, USA			Turkey, South Korea, Indonesia	
40	Poster presentation	UNIABDN	Biocompatibility of DC magnetron-sputtered TiO2 coatings with nano-scale morphology and controlled phase composition on glass substrates	27th November – 2nd December 2016	MRS (Materials Research Society) Fall Meeting, Boston, USA	Scientific Community	>1000	Europe, Japan, USA, Canada, Brazil, Turkey, South Korea	presented
41	Oral presentation	UNIABDN	The Role Of Nanoparticles In Developing The Next Generation Medical Devices	4-9th September 2016	Nanoscience meets Metrology. International Summer School. Torino. Italy.	Scientific Community	40	EU countries	presented
42	Conference Talk	DTU	Analyse Photocatalytic activity of Titanium Dioxide Coatings on conducting substrates	28 Sept-01 Oct 2016	Functional Energy Materials Zing Conference, Dubrovnik, Croatia	Scientific Community	<100	France, Italy, UK, Canada, Denmark, Norway, Germany	presented

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
43	Oral presentation	DTI	Photocatalytic TiO2 coatings optimised for industrial-scale magnetron sputtering equipment	10th of September 2015	Guimarães, Portugal	Scientific community (higher education, Research)	30	Portugal, Denmark, United Kingdom, France, Greece, Spain, Italy, Czech Republic, Sweden, Germany	Presente d
44	Poster	DTI	Setup for measuring photocatalytic activity of TiO2 coatings by conversion of gaseous organic substrates into CO2	11thof September 2015	Guimarães, Portugal	Scientific community (higher education, Research)	30	Portugal, Denmark, United Kingdom, France, Greece, Spain, Italy, Czech Republic, Sweden, Germany	Presente d
45	Poster	IUF	Nanotoxicological assessment of shape-engineered titanium dioxide nanoparticles	12 – 12 March 2015	81st Annual Congress of the German Society for Experimental and	Scientific Community	>500	Germany	presente d

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
					Clinical Pharmacology and Toxicology (DGPT), Kiel, Germany				
46	Presentation	IUF	Nanotoxicological assessment of shape-engineered titanium dioxide nanoparticles	27 – 31 July 2015	International Summer Workshop NANOSCIENCE meets METROLOGY, Erice, Italy	Scientific Community,	54	EU	presente d
47	Poster	IUF	Toxic and inflammatory effects of shape-engineered titanium dioxide nanoparticles in NR8383 rat alveolar macrophages	29 February – 3 March 2016	German Pharm-Tox Summit 2016, Berlin, Germany	Scientific Community	>500	Germany	presente d
48	Presentation + Poster	IUF	Toxicological assessment of shape-engineered titanium dioxide nanoparticles	1 – 4 June 2016	8th International Nanotoxicology Congress, Boston, USA	Scientific Community, Industry,polic y makers	>300	EU-countries (e.g. Germany, UK, Italy, France, Belgium, Denmark, Netherlands	presente d

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
								), Switzerland, Turkey, USA, Canada, China, Japan,	
49	Lecture	IUF	Nanotoxicology - mechanisms and metrics	4 – 9 September 2016	International Summer School Nanoscience meets Metrology.. Torino, Italy	Scientific Community	40	..	Presented
50	Presentation (+ Scientific session chair)	IUF	Toxicological assessment of shape-engineered titanium dioxide nanoparticles	26-30 September 2016	11th International Particle Toxicology Symposium (IPTC11), Singapore	Scientific Community	>100	EU (e.g. Germany, UK, Italy, France, Netherlands, Belgium), USA, Canada, China, Japan, India, Taiwan, South Korea, Singapore,...	Presented

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES									
No.	Type of activities	Main leader	Title	Date/Period	Place	Type of audience	Size of audience	Countries addressed	Status
51	Lecture	IUF	Nanotoxicology	27 – 29 Oct 2016	Workshop Nanomedicine and contrast agents. Maastricht, The Netherlands	Scientific community, industry,	15	Netherlands, Germany, Switzerland, UK, Sweden	presented
52	Poster	IK4-TEKNIKER	Fenton/photo-fenton heterogenous processes for the removal of azodyes	25-28 June 2014	8th European Meeting on Solar Chemistry and Photocatalysis: Environmental applications, Thessaloniki				presented

5.2 Section B

5.2.1 Part B1

Not applicable, the project did not produce any patents, trademarks or registered designs.

5.2.2 Part B2

Type of Exploitable Foreground	Description of Exploitable foreground	Confidential Yes/No	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
OTHERS	HRGO/TiO2 particles to use in composites[1]	Yes		HRGO/TiO2	* Materials * Polymer industry	12-24 moths	Study of freedom to operate before patenting	AVANZARE
OTHERS	Sol-gel synthesis of TiO2 with controlled features[1]	Yes		TiO2 nanoparticles	* Materials * Metrology * Polymer industry	Commercial at small quantities	Internal know-how	Avanzare, Tekniker
OTHERS	Work item proposal to CEN/TC 352 “Nanotechnologies”: Characterization of the surface TiO2 nanoparticles by FT-IR spectroscopy under a controlled atmosphere[2]	NO		FT-IR measurement method	1. Production of Inorganic nanoparticles	31/12/2018	None	UNITO UNI CEN/TC 352

OTHERS	Aqueous suspensions of TiO_2 nanoparticles of three different shapes: bipyramids with a low truncation, rod-like and sheets, each with size within defined limits[3]	NO		Three types of TiO_2 Nanoparticles	1. Photocatalysis 2. Photo-voltaic solar cells 3. Nanotoxicological tests	31/12/2017	None	Beneficiary: UNITO Beneficiary: RD Beneficiary: BAM
OTHERS	Portable photoreactor for fast, traceable and in situ measuring of photocatalytic activity in the gas-solid regime[4]	YES	31/12/2018	Equipment for photocatalysis in gas-solid regime	1. Photocatalysis	31/12/2017	None	Beneficiary: UNITO Licence to equipment manuf. FONDERIA MESTIERI, Turin, Italy
OTHERS	Miniature photoreactor for fast, accurate and traceable measurement	YES	31/12/2018	Equipment for photocatalysis in liquid-solid regime	1. Photocatalysis	31/12/2017	None	Beneficiary: UNITO Licence to equipment manuf. FONDERIA MESTIERI, Turin, Italy

	of photocatalytic activity in the liquid-solid regime[5]							
PATENT	Femtosecond laser ablation in liquid: Novel system design for scale-up of LA equipment for generation of NPs[6]	Yes	-	Industrial for laboratory supplies	Scientific/ R&D	2020	Patent is planned	Applied Research Institute for Prospective Technologies
OTHERS	New knowledge: Experimental and computed data and the developed soft models for HT and SG syntheses[7]	No	No	University courses	1. High education training	2018 and the next years	None	Beneficiary: students (bachelor and master) at Politehnica University of Bucharest - Faculty of Applied Chemistry and Material Science, Department Chemistry Engineering
OTHERS	Certified Reference Material: Certification of selected properties of	No	n. a.	Certificate	Measurement facilities – all analytical methods which need reference	2018	None	BAM

	TiO2 nanoparticles or their assemblies (layers)[8]				materials for calibration and validation purposes			
OTHERS	Measurement set-up and uncertainty: Spectral Irradiance[9]	NO	01/01/2015	Industrial measurement service: Characterization of UV light sources	1. Medical (UV sterilization) 2. Industrial inspection (LED manufacturing)	Established, already customer orders and/or R&D projects existing	None	None
OTHERS	Measurement set-up and uncertainty: Youngs Modulus of NPs[9]	NO	01/01/2017	Industrial measurement service: Elasticity of NP material	1. Pharmaceutics (powder particles in medicine)	Established, already customer orders and/or R&D projects existing	None	None
OTHERS	Measurement set-up and uncertainty: Kelvin Probe for NP applications[9]	NO	01/01/2017	Industrial measurement service: Kelvin Probe	1. Industrial inspection (photocatalytic services)	Established, already customer orders and/or R&D projects existing	None	None
OTHERS	Measurement set-up and uncertainty: NP size and morphology[9]	NO	01/01/2016	Industrial measurement service: Particle size and morphology	1. Industrial inspection (certification of reference particles)	Established, already customer orders and/or R&D projects existing	None	None

OTHERS	Establishment of Traceability for workfunction property of metals and metal oxides[9]	NO	01/01/2017	Certification service: photolytic activity of reference standards	1. Reference material for Industry	Established	None	AVANZARES (NP production) IK4TEKNIKER (Sample production) SOLARONIX (Sale&Marketing)

1 Thanks to SetNanometro project, Avanzare has studied the scale-up of sol-gel TiO2 nanoparticles, following the advices of Tekniker. The obtained results can be exploited in different markets in order to create new materials with enhanced photocatalytic activity, even they can be used in metrology to be used as an standard for the photocatalytic activity. In addition, the nanoparticles will help to create more degradable polymers for plastics with defined short lifetime such as plastic bags, or small containers for food.

At this moment, Avanzare will protect the knowledge as internal know-how and if the product received an strong interest for the industry, patent could be considered.

The product is ready to be commercialized at small scale, although achieving bigger scale is needed in order to explore markets such as polymers.

Avanzare will release the product in their online shop along next month, with the idea of increasing their portfolio of products. TiO2 nanoparticles will be sold separately and combined with graphene. Combined with graphene will let prepare suitable conductive composites that will combine the conductivity of graphene together with the photocatalytic activity of the titanium nanoparticles. During 1-2 years, Avanzare will test the interest of the market with different marketing strategies: mainly attendance to specialized fairs and use of the commercial network of the company. After this period, the product will be properly placed as industrial product for the company.

2 Exploitable foreground: Characterization of the surface TiO2 nanoparticles by FT-IR spectroscopy under a controlled atmosphere

The purpose of this exploitable foreground is to provide an “on site” cheap and fast system for the assessment of surface structure and properties of TiO2 nanoparticles to industry, and SMEs in particular, in addition to imaging by electron microscopy (EM), attaining information at molecular level. The initial investment for the equipment and the yearly maintenance are of the order of 104 and 103 € , respectively, thus significantly lower than those of the order of 105-106 and 104 €, respectively, required for EM. To attain the exploitation of this foreground, a process aimed to its acceptance by regulatory bodies was started. The Italian UNI National Committee “Nanotechnology was contacted by the Exploitation Leader of

SETNanoMetro, as a first step for the proposal of a work item to CEN/TC 352. Nor particular IPR measures neither further research are required at present. This method proposed by SETNanoMetro is expected to positively impact on the possibility for SMEs producing TiO2 NPs to have a cheap, fast and autonomous access (with respect to the access to specialized EM laboratories) to a traceable assessment of the surface structure of the NP they produce.

3 Exploitable foreground: TiO2 nanoparticles with defined shape and size

This exploitable foreground is intended to provide TiO2 nanoparticles (NP) of interest as reference materials for industries, SMEs, research centers. The interest is based on the highly defined bulk structure, shape and size of the titanium dioxide NPs proposed, resulting from the controlled and reproducible preparation methods developed by SETNanoMetro. To this aim, the information about availability and cost of these products of SETNanoMetro will be disseminated posting the relevant information on the websites of the project (www.setnanometro.eu) and of two of the SMEs in the project consortium, namely Solaronix (www.solaronix.com) and Avanzare (www.avanzare.es).

These products of SETNanoMetro will help enterprises producing oxide nanoparticles, and titanium dioxide nanoparticles in particular, to control the correctness of their implementation of standard operative procedures (SOPs) for the production and/or characterization of the nanoparticles of those type they could produce.

4 Exploitable foreground: Gas-solid photoreactor

This exploitable foreground is intended to provide a fast, cheap and traceable procedure and apparatus for the measurement of the photocatalytic activity in the gas solid regime of nanoparticles films, paints, concrete and other photocatalytic surfaces. The reactor is portable and designed also for in situ measurements. The fluid-dynamic of the photoreactor was designed to measure the intrinsic photocatalytic activity of the material, without problems related to the mass transfer resistances. The measure is carried out within minutes and not hours, as required by ISO 22197-1: 2007. This apparatus is of interest for industries, SMEs, research centers that need to measure with a fast, reliable and traceable method the photocatalytic activity of surfaces and films. In situ measurements allow to establish the durability of the photocatalytic material. The companion exploitable foreground represented by TiO2 nanoparticles with defined shape and size will allow the operators to control the accuracy of the measurement. The information about availability and cost of these products of SETNanoMetro will be disseminated posting the relevant information on the website of the project (www.setnanometro.eu) and through "Fonderia Mestieri SrL" (www.fonderiamestieri.com). This device will help to develop, implement, control the production, deploy and in situ asses the durability photocatalytic materials in the gas solid regime.

5 Exploitable foreground: Liquid-solid photoreactor

This exploitable foreground is intended to provide a fast, cheap and traceable procedure and apparatus for the measurement of the photocatalytic activity in the liquid solid regime of photocatalytic nanoparticles supsensions and films. The fluid-dynamic of the photoreactor was designed to measure the intrinsic photocatalytic activity of the material, without problems related to circulation of liquid in the reactor. The measure is carried out within minutes and not hours, as required by ISO standards. This apparatus is of interest for industries, SMEs, research centers that need to measure with a fast, reliable and traceable method the photocatalytic activity of potocatalyst nanoparticles and films. The companion exploitable foreground represented by TiO2 nanoparticles with defined shape and size will allow the operators to control the accuracy of the measurement. The information about availability and cost of these products of SETNanoMetro will be disseminated posting the relevant information on the website of the project (www.setnanometro.eu) and through "Fonderia Mestieri SrL" (www.fonderiamestieri.com). This device will help to develop, implement, control the production, deploy photocatalytic materials by ensuring a reliable, accurate and traceable measurement of photocatalytic activity in the liquid solid regime (e.g. for water purification).

[6] Commercialization of NPs obtained by laser ablation in liquid is restricted by low nanoparticle (NP) quantities produced (especially for femtosecond lasers).

A novel laser ablation system design was proposed for nanoparticle generation scale up purposes. Laser system used should be equipped with high power laser, a beam splitter and automation system. High power laser is needed to keep the same power of single sub-beam after beam splitter to maintain the same ablation conditions as it is used up to now. Equipment used for realization of this idea (powerful laser, beam splitter, opto-mechanical handling, etc.) must be available at the market. Such system would provide numbers of NPs high enough at least for applications at other fields of research.

[7] Students shall get access to new research results in the field of complex chemical processes. The foreground, consisting of experimental and computed data and the developed soft models for HT and SG syntheses will be used, starting with 2018, by 2 members of WP2 team, as new elements and relevant examples for particular types of chemical processes, for their courses in the field of chemical engineering studies: "Data Analysis and Experimental Design", and/or "Numerical Methods and Optimisation". The impact is strengthening the link between research and high education training.

[8] The exploitable foreground consists of a certificate attesting well-defined properties of TiO2 nanoparticles and layers to be used as reference values for calibration of instruments or validation of analytical methods. TiO2 particulate material properties agreed by the SETNanoMetro consortium which may be certified are (in priorities):
Size and shape distribution of TiO2 nanoparticles; the bipyramidal UT001 has priority, other shapes like platelets, acicular and spherical follow;
Specific surface area TiO2 nanoparticles; the bipyramidal UT001 powder has priority,
Crystallinity expressed as quantitative fractions of polymorphs; the bipyramidal UT001 powder has priority,
Thickness, mass coating and density of TiO2 porous layers; layers deposited by pulsed D.C. magnetron sputtering have priority,
Porosity and inner (pore) specific surface of TiO2 porous layers; layers deposited by pulsed D.C. magnetron sputtering have priority
Elemental composition of TiO2 porous layers; layers deposited by pulsed D.C. magnetron sputtering have priority.

With respect to the certification of reference materials BAM is accredited per ISO Guide 34: 2009 "General requirements for the competence of reference materials producers".

The basis for the certification of size and shape distribution of bipyramidal TiO2 nanoparticles UT001 is given by the data obtained from an inter-laboratory comparison organized by BAM within ISO/TC 229 'Nanotechnologies' / Joint Working Group 2 'Measurement and characterization' (with 16 laboratories with competence in the field of nanoparticle size measurement by electron microscopy).

9 These exploitables are almost exclusively connected with in-house measurement services. The foreground knowledge consists of know-how generated during the set-up of sophisticated measurement installations, along with the theoretical modelling of the physics behind the measurement process. These are the typical requirements to establish an uncertainty budget, which along with the establishment of tracebility provides the key elements for metrology. The services have been established during the project, and are currently attracting the first customers' attentions. IPR measures are not intended, as the instrumentation and set-up is too specialized in order to be copied without sever investments both in equipment as well as staff training at an academic level.

Further research is not necessary. However, the services and the foreground knowledge will enter future R&D applications and project, and are likely to be further developed and enhanced.

The annual income is estimated to 20 k€ for the customer services, and 200 k€ as part of R&D projec

6 Report on societal implications

Replies to the following questions will assist the Commission to obtain statistics and indicators on societal and socio-economic issues addressed by projects. The questions are arranged in a number of key themes. As well as producing certain statistics, the replies will also help identify those projects that have shown a real engagement with wider societal issues, and thereby identify interesting approaches to these issues and best practices. The replies for individual projects will not be made public.

A General Information *(completed automatically when **Grant Agreement number** is entered.*	
Grant Agreement Number:	604577
Title of Project:	Shape-engineered TiO2 nanoparticles for metrology
Name and Title of Coordinator:	Andrea Mario Rossi, Ph.D

B Ethics	
1. Did your project undergo an Ethics Review (and/or Screening)? • If Yes: have you described the progress of compliance with the relevant Ethics Review/Screening Requirements in the frame of the periodic/final project reports? Special Reminder: the progress of compliance with the Ethics Review/Screening Requirements should be described in the Period/Final Project Reports under the Section 3.2.2 *'Work Progress and Achievements'*	***NO***
2. Please indicate whether your project involved any of the following issues (tick box) :	
RESEARCH ON HUMANS	
• Did the project involve children?	
• Did the project involve patients?	
• Did the project involve persons not able to give consent?	
• Did the project involve adult healthy volunteers?	
• Did the project involve Human genetic material?	
• Did the project involve Human biological samples?	
• Did the project involve Human data collection?	
RESEARCH ON HUMAN EMBRYO/FOETUS	
• Did the project involve Human Embryos?	
• Did the project involve Human Foetal Tissue / Cells?	
• Did the project involve Human Embryonic Stem Cells (hESCs)?	
• Did the project on human Embryonic Stem Cells involve cells in culture?	
• Did the project on human Embryonic Stem Cells involve the derivation of cells from Embryos?	
PRIVACY	
• Did the project involve processing of genetic information or personal data (eg. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?	

• Did the project involve tracking the location or observation of people?	
RESEARCH ON ANIMALS	
• Did the project involve research on animals?	
• Were those animals transgenic small laboratory animals?	
• Were those animals transgenic farm animals?	
• Were those animals cloned farm animals?	
• Were those animals non-human primates?	
RESEARCH INVOLVING DEVELOPING COUNTRIES	
• Did the project involve the use of local resources (genetic, animal, plant etc)?	
• Was the project of benefit to local community (capacity building, access to healthcare, education etc)?	
DUAL USE	
• Research having direct military use	
• Research having the potential for terrorist abuse	

C Workforce Statistics

3. Workforce statistics for the project: Please indicate in the table below the number of people who worked on the project (on a headcount basis).

Type of Position	Number of Women	Number of Men
Scientific Coordinator	1	1
Work package leaders	2	9
Experienced researchers (i.e. PhD holders)	31	41
PhD Students	8	3
Other	7	7

4. How many additional researchers (in companies and universities) were recruited specifically for this project?	
Of which, indicate the number of men:	10

D Gender Aspects

5. Did you carry out specific Gender Equality Actions under the project?	○ x	Yes No

6. Which of the following actions did you carry out and how effective were they?

		Not at all effective → Very effective
❑	Design and implement an equal opportunity policy	○ ○ ○ ○ ○
❑	Set targets to achieve a gender balance in the workforce	○ ○ ○ ○ ○
❑	Organise conferences and workshops on gender	○ ○ ○ ○ ○
❑	Actions to improve work-life balance	○ ○ ○ ○ ○
x	Other:	An equal opportunity policy has been part of the standard recruiting strategy of the partners.

7. Was there a gender dimension associated with the research content – i.e. wherever people were the focus of the research as, for example, consumers, users, patients or in trials, was the issue of gender considered and addressed?

○ Yes- please specify

x No

E Synergies with Science Education

8. Did your project involve working with students and/or school pupils (e.g. open days, participation in science festivals and events, prizes/competitions or joint projects)?

x Yes- please specify: Summer school for PhD students

○ No

9. Did the project generate any science education material (e.g. kits, websites, explanatory booklets, DVDs)?

○ Yes- please specify

x No

F Interdisciplinarity

10. Which disciplines (see list below) are involved in your project?

○ Main discipline[1]: 1,2 and 3

○	Associated discipline1: 1.1, 1.2, 1.3	○ ○	Associated discipline2:2.2, 2.3 Associated discipline3: 3.1

G Engaging with Civil society and policy makers

11a Did your project engage with societal actors beyond the research community? *(if 'No', go to Question 14)*	X ○	Yes No

[1] Insert number from list below (Frascati Manual).
[2] Open Access is defined as free of charge access for anyone via Internet.

11b If yes, did you engage with citizens (citizens' panels / juries) or organised civil society (NGOs, patients' groups etc.)?

- x No
- ○ Yes- in determining what research should be performed
- ○ Yes - in implementing the research
- ○ Yes, in communicating /disseminating / using the results of the project

11c In doing so, did your project involve actors whose role is mainly to organise the dialogue with citizens and organised civil society (e.g. professional mediator; communication company, science museums)?	○ X	Yes No

12. Did you engage with government / public bodies or policy makers (including international organisations)

- ○ No
- ○ Yes- in framing the research agenda
- ○ Yes - in implementing the research agenda
- x Yes, in communicating /disseminating / using the results of the project

13a Will the project generate outputs (expertise or scientific advice) which could be used by policy makers?

- ○ Yes – as a **primary** objective (please indicate areas below- multiple answers possible)
- ○ Yes – as a **secondary** objective (please indicate areas below - multiple answer possible)
- x No

13b If Yes, in which fields?

Agriculture		Energy		Human rights	
Audiovisual and Media		Enlargement		Information Society	
Budget		Enterprise		Institutional affairs	
Competition		Environment		Internal Market	
Consumers		External Relations		Justice, freedom and security	
Culture		External Trade		Public Health	
Customs		Fisheries and Maritime Affairs		Regional Policy	
Development Economic and Monetary Affairs		Food Safety		Research and Innovation	
Education, Training, Youth		Foreign and Security Policy		Space	
Employment and Social Affairs		Fraud		Taxation	
		Humanitarian aid		Transport	

13c If Yes, at which level?

- ○ Local / regional levels
- ○ National level
- ○ European level
- ○ International level

H Use and dissemination

14. How many Articles were published/accepted for publication in peer-reviewed journals?	**16**
To how many of these is open access[2] provided?	**3**
How many of these are published in open access journals?	**0**
How many of these are published in open repositories?	
To how many of these is open access not provided?	**12**
Please check all applicable reasons for not providing open access:	
❑ publisher's licensing agreement would not permit publishing in a repository ❑ no suitable repository available X no suitable open access journal available ❑ no funds available to publish in an open access journal ❑ lack of time and resources ❑ lack of information on open access ❑ other[3]: ……………	

15. How many new patent applications ('priority filings') have been made? *("Technologically unique": multiple applications for the same invention in different jurisdictions should be counted as just one application of grant).*	

16. Indicate how many of the following Intellectual Property Rights were applied for (give number in each box).	Trademark	
	Registered design	
	Other	

17. How many spin-off companies were created / are planned as a direct result of the project?	
Indicate the approximate number of additional jobs in these companies:	

18. Please indicate whether your project has a potential impact on employment, in comparison with the situation before your project:

❑	Increase in employment, or	X	In small & medium-sized enterprises
❑	Safeguard employment, or	❑	In large companies
❑	Decrease in employment,	❑	None of the above / not relevant to the project
❑	Difficult to estimate / not possible to quantify		

[2] Open Access is defined as free of charge access for anyone via Internet.
[3] For instance: classification for security project.

19. For your project partnership please estimate the employment effect resulting directly from your participation in Full Time Equivalent (*FTE = one person working fulltime for a year*) jobs:	*Indicate figure:*
Difficult to estimate / not possible to quantify	X

I Media and Communication to the general public

20. As part of the project, were any of the beneficiaries professionals in communication or media relations?

○ Yes X No

21. As part of the project, have any beneficiaries received professional media / communication training / advice to improve communication with the general public?

○ Yes X No

22 Which of the following have been used to communicate information about your project to the general public, or have resulted from your project?

X	Press Release	X	Coverage in specialist press
❑	Media briefing	X	Coverage in general (non-specialist) press
❑	TV coverage / report	X	Coverage in national press
X	Radio coverage / report	❑	Coverage in international press
X	Brochures /posters / flyers	X	Website for the general public / internet
X	DVD /Film /Multimedia	X	Event targeting general public (festival, conference, exhibition, science café)

23 In which languages are the information products for the general public produced?

❑	Language of the coordinator	X	English
❑	Other language(s)		

Question F-10: Classification of Scientific Disciplines according to the Frascati Manual 2002 (Proposed Standard Practice for Surveys on Research and Experimental Development, OECD 2002):

FIELDS OF SCIENCE AND TECHNOLOGY

1. NATURAL SCIENCES
1.1 Mathematics and computer sciences [mathematics and other allied fields: computer sciences and other allied subjects (software development only; hardware development should be classified in the engineering fields)]
1.2 Physical sciences (astronomy and space sciences, physics and other allied subjects)
1.3 Chemical sciences (chemistry, other allied subjects)
1.4 Earth and related environmental sciences (geology, geophysics, mineralogy, physical geography and other geosciences, meteorology and other atmospheric sciences including climatic research, oceanography, vulcanology, palaeoecology, other allied sciences)
1.5 Biological sciences (biology, botany, bacteriology, microbiology, zoology, entomology, genetics, biochemistry, biophysics, other allied sciences, excluding clinical and veterinary sciences)

2 ENGINEERING AND TECHNOLOGY

2.1 Civil engineering (architecture engineering, building science and engineering, construction engineering, municipal and structural engineering and other allied subjects)

2.2 Electrical engineering, electronics [electrical engineering, electronics, communication engineering and systems, computer engineering (hardware only) and other allied subjects]

2.3. Other engineering sciences (such as chemical, aeronautical and space, mechanical, metallurgical and materials engineering, and their specialised subdivisions; forest products; applied sciences such as geodesy, industrial chemistry, etc.; the science and technology of food production; specialised technologies of interdisciplinary fields, e.g. systems analysis, metallurgy, mining, textile technology and other applied subjects)

3. MEDICAL SCIENCES

3.1 Basic medicine (anatomy, cytology, physiology, genetics, pharmacy, pharmacology, toxicology, immunology and immunohaematology, clinical chemistry, clinical microbiology, pathology)

3.2 Clinical medicine (anaesthesiology, paediatrics, obstetrics and gynaecology, internal medicine, surgery, dentistry, neurology, psychiatry, radiology, therapeutics, otorhinolaryngology, ophthalmology)

3.3 Health sciences (public health services, social medicine, hygiene, nursing, epidemiology)

4. AGRICULTURAL SCIENCES

4.1 Agriculture, forestry, fisheries and allied sciences (agronomy, animal husbandry, fisheries, forestry, horticulture, other allied subjects)

4.2 Veterinary medicine

5. SOCIAL SCIENCES

5.1 Psychology

5.2 Economics

5.3 Educational sciences (education and training and other allied subjects)

5.4 Other social sciences [anthropology (social and cultural) and ethnology, demography, geography (human, economic and social), town and country planning, management, law, linguistics, political sciences, sociology, organisation and methods, miscellaneous social sciences and interdisciplinary , methodological and historical S1T activities relating to subjects in this group. Physical anthropology, physical geography and psychophysiology should normally be classified with the natural sciences].

6. HUMANITIES

6.1 History (history, prehistory and history, together with auxiliary historical disciplines such as archaeology, numismatics, palaeography, genealogy, etc.)

6.2 Languages and literature (ancient and modern)

6.3 Other humanities [philosophy (including the history of science and technology) arts, history of art, art criticism, painting, sculpture, musicology, dramatic art excluding artistic "research" of any kind, religion, theology, other fields and subjects pertaining to the humanities, methodological, historical and other S1T activities relating to the subjects in this group]

1. FINAL REPORT ON THE DISTRIBUTION OF THE EUROPEAN UNION FINANCIAL CONTRIBUTION

This report shall be submitted to the Commission within 30 days after receipt of the final payment of the European Union financial contribution.

Report on the distribution of the European Union financial contribution between beneficiaries

Name of beneficiary	Final amount of EU contribution per beneficiary in Euros
1.	
2.	
n	
Total	