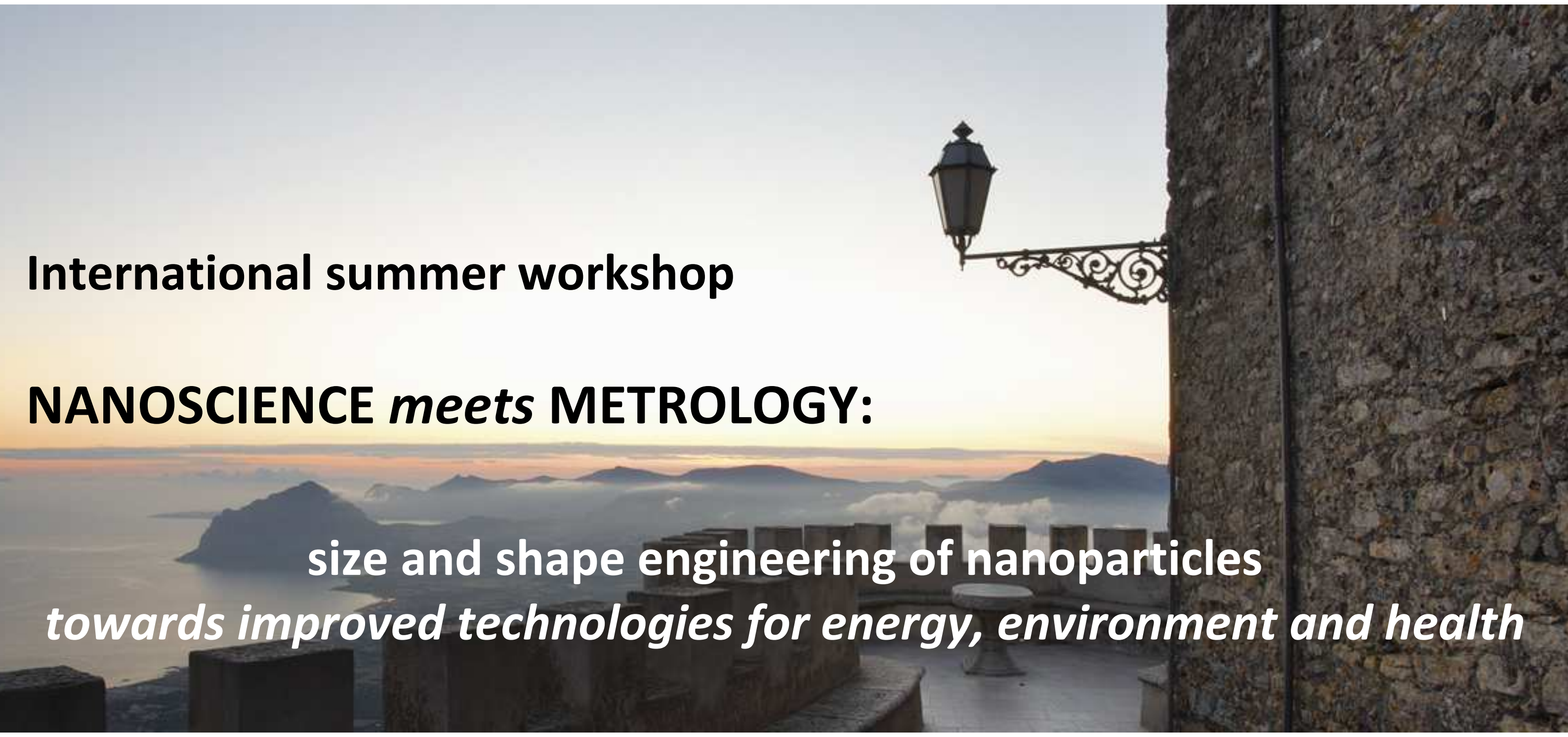
SEVENTH FRAMEWORK PROGRAMME

Andrea M. Rossi Gianmario Martra Chiara Portesi



International summer workshop

NANOSCIENCE *meets* METROLOGY:

size and shape engineering of nanoparticles *towards improved technologies for energy, environment and health*

Book of Abstracts

Programme

27th-31st July 2015, Erice - Sicily (Italy)
Ettore Majorana Foundation and Centre for Scientific Culture

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Book of Abstracts

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The Workshop is organized by the

SETNanoMetro

EU/FP7 project

www.setnanometro.eu

SEVENTH FRAMEWORK
PROGRAMME

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Shape-**e**ngineered **T**iO_2 **nano**particles for **metro**logy of functional properties: setting design rules from material synthesis to nanostructured devices

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 detection, characterization and analysis of nanoparticles

In the framework of the SETNanometro project, the use of various measurement techniques for the determination of the NPs properties will allow to move from the currently used "trial and error" approach toward the development of
well defined and controlled protocols for the production of TiO_2 NPs

A particular care will be devoted to the establishment of
correct metrological traceability chains in order to ensure the reliability of the results

The lact 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 measurements at nanoscale

Follow the SETNanoMETRO activities at *www.setnanometro.eu !*

The SETNanoMetro consortium

INRiM ISTITUTO NAZIONALE DI RICERCA METROLOGICA

DFM Danish National Metrology Institute

BAM Federal Institute for Materials Research and Testing

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Summary

Abstracts

Acknowledgment

Editors are obliged to Mr. Marco Fabbiani, PhD student,
the volunteer who constituted the “one-man editorial production staff” of this book

Foreword

The international summer workshop **"NANOSCIENCE *meets* METROLOGY: size and shape engineering of nanoparticles. *Towards improved technologies for energy, environment and health*"** represents a dissemination action of the **FP7 EU project SETNanoMetro** (www.setnanometro.eu), that the project consortium would offer to the scientific community as a possibility of cross-fertilization among complementary sectors of modern nanoscience and nanotechnology. But what about the origin of this project and then of this workshop?
The Roadmap Report on Nanoparticles (NanoRoadMap FP6 project 2004-2006) indicated that "the manufacture of NPs with precise size and crystal orientation is among the **futuristic applications** that could enter the basic /applied R&D phases by **2010-2015**"

….now, **the time has now come**, and this workshop, inspired by the objectives and expected impacts of SETNanoMetro, was intended for all scientists and technologists interested in:
1. production of nanoparticles with defined shape and size
2. measurement of their structural, morphological and surface features
3. controlled assembly and/or aggregation of nanoparticles on supports (film formation)
4. measurement of functional performance of nanoparticles , dispersed or in a supported form, for applications in three technological domains :

environmental protection and remediation, energy, health

In particular, the workshop would represent a crossroad resulting from the intersection between nanoscience/nanotechnology and metrology, where several issues relevant for the European Research Area are emerging:

- ✓ *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;*
- ✓ *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 (for example, the ability to design nano-coatings or nano-enabled coatings with specific performance properties).*

The response of the European scientific community resulted in a **programme** with an introductory **plenary lecture (PL), 36 oral presentation**, organized in **6 sessions (+ a "special" one),** each opened by a **keynote lecture (KN)**, and in **a poster session with 11 contributions**.

Invited lectures will be given by the following distinguished scientists from universities, research centres, metrological institutes, private companies, who are sincerely acknowledged by the SETNanoMetro consortium for having accepted to contribute to enrich the scientific programme of the workshop:

Dr. Roberto Comparelli (PL), University of Bari and CNR (Italy)
Prof. Corinne Chanéac (KN), Laboratoire de la Chimie de la Matière Condensée de Paris (France)
Prof. Rodrigo Moreno (KN), Institute of Ceramics and Glass, Madrid (Spain)
Dr. Wolfram Bremser (KN), BAM Federal Institute for Materials Research and Testing, (Germany)
Dr. Renaud Demadrille (KN), Institut Nanosciences et Cryogénie (France)
Dr. Theis Reenberg (KN), Photocat A/S (Denmark)
Dr Wim de Jong (KN), Netherlands National Institute of Public Health and the Environment

Andrea M. Rossi
(coordinator of SETNanoMetro)
Chiara Portesi
Gianmario Martra

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ABSTRACTS

(PL)

COLLOIDAL NANOCRYSTALS AT WORK: ORIGINAL OPPORTUNITIES FOR FUNCTIONAL MATERIALS

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ABSTRACT

Nanostructured materials (metals, semiconductors, nanocomposites, mesoporous solids) represent a new class of materials, showing designable and tunable properties. Nanomaterial size/shape dependent physical-chemical properties as well as quantization effect in nano-semiconductors and charging effect in metal nanoparticles (NPs) provide the opportunity to develop innovative materials for heterogeneous catalysis,[1] environmental protection,[2] energy harvesting and conversion[3] and nanomedicine.[4] A precise control on size and shape of the nanoparticles is crucial to *a priori* design their final properties and to tailor the peculiar characteristics of nanomaterials as a function of their final application. Interestingly, modern nanochemistry offers to opportunity to prepare multifunction heterostructures merging in one material different chemical domains thus finally obtaining nanostructured materials with unprecedented physical-chemical properties. Another crucial point is the ability to access nanoparticle properties for devices fabrication. In this view, assembly procedures allow the formation of original ordered state of matter and the fabrication of 2/3 D patterned micro and nanostructure, representing a promising route for producing functional materials and for processing and integrating the nanoparticles in macroscopic systems, thus bridging the gap between nanoscopic and mesoscopic scale.
This presentation will focus on modern synthetic approach to obtain nanostructured materials with designed size and shape.[5] Post-synthetic surface engineering and assembly procedures for integration in devices will be reviewed.[6] Some examples of applications of nanostructured materials and their assemblies in environmental protection and remediation,[7] energy conversion[8] and nanomedicine will be outlined.[9]

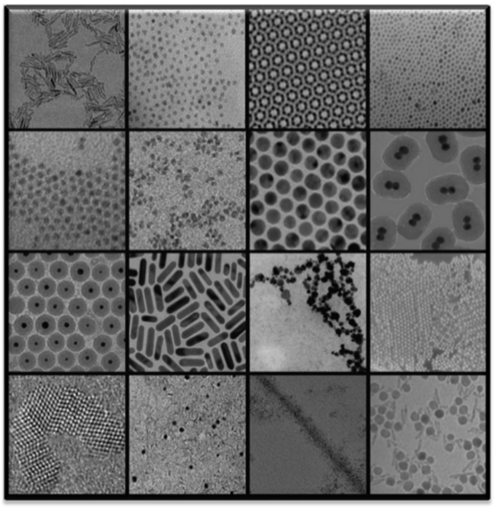

Figure1. Some examples of colloidal nanocrystals and heterostructures with designed size, shape and chemical composition.

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Notes

Session 1 (S1)

Preparation of nanoparticles

(KN-S1)

DESIGN OF METAL OXIDE NANOPARTICLES USING SOFT CHEMISTRY

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ABSTRACT

The chemistry of metallic cations in aqueous solution is a relevant method to the elaboration of nanometric scale metallic oxides. This method is extremely versatile and allows one to control many characteristics of materials like iron, aluminium and titanium oxides, in particular, the crystalline structure for polymorphic compounds, the particles size and shape. The main parameters being more relevant are the acidity of solution, the presence of specific anions, and the temperature. The synthesis process has been optimised in order to study each parameter separately. Two synthetic routes are currently being developed within the LCMCP team involving the nucleation-growth of the particles either by alkalization or by thermolysis of molecular precursors. The crystalline phases obtained by alkalinization are often metastable phases and we have shown that the size and morphology of particles were governed by surface energy. For thermolysis, the formation of solid is slower due to the slower generation of precursors of the solid and leads to the crystallization of a thermodynamically stable phase. In this case, the solubility and precursor concentration are the key parameters that will control the characteristics of the particles.

We have shown in the case of magnetite and anatase particles that the particles size decreases as the pH of precipitation departs more and more from the point of zero charge, PZC. For others materials such as brucite (Mg(OH)2) and boehmite (⍰-AlOOH), the variation of morphology occurs. These examples bring decisive experimental arguments allowing connecting the size and shape of nanoparticles to the acidity of synthesis medium. We have also investigated some experiments using weak complexing molecules and we have shown that the use of small quantity of polyols allowed also to tune surface energy for each crystallite faces involving some change in aspect ratio for a given particle shape.

Notes

(O1-S1)

FLEXIBLE OXIDE SURFACES

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ABSTRACT

The interaction of oxide surfaces with water is a pivotal issue regarding oxide surfaces but its study is still in infancy. For example, the structure of hydroxylated zinc oxide surfaces is vividly debated [1] while OH sites are not identified yet on α-Al2O3(0001) though H_2O dissociation is established experimentally [2] and theoretically.[3] As for MgO(100), its interaction with H_2O appears paradoxical. The prediction that (100) surface do not dissociate H_2O is contradicted by the claim that MgO(100) films do it and by the observation of hydroxylated MgO(100) surfaces in near ambient conditions. Regarding the former point, we have shown that isolated water molecules are not dissociated by stoichiometric (100) surfaces of MgO, whatever their support.[4] Indeed, MgO(100) do dissociate H_2O under pressure > 10^{-3} Pa, [5] presumably due to cooperative H_2O action.[6] In a way which might be in line with that, MgO(100) transforms upon adsorption-desorption cycles. Its ability to dissociate water is progressively inhibited while revealing <110> features which point to the formation of polar facets.[5] Consistently, upon contact with H_2O, cubic MgO nanocrystallites limited by (100) facets transform into octahedra with polar (111) facets – OH-stabilized – via an intermediate situation with metastable (110) facets of kinetic origin (Figure 1).[7]

Supported by the earlier suggestion that the chemical activity of the MgO surface involves polar (111) facets [8], the above findings question the representation of MgO surfaces by a Kossel model [9] (stacking of cubes (atoms)) that pictures all surface features (terraces, steps, kinks …) via a unique {100} orientation. There is increasing evidences that the reactivity of MgO(100) often involves metastable or polar facets that are not made of stacked (100) facets.[10] More generally, many oxides are expected to show surface profiles that depend on environment in a similar way as metal nanoparticles that are much studied in such context.

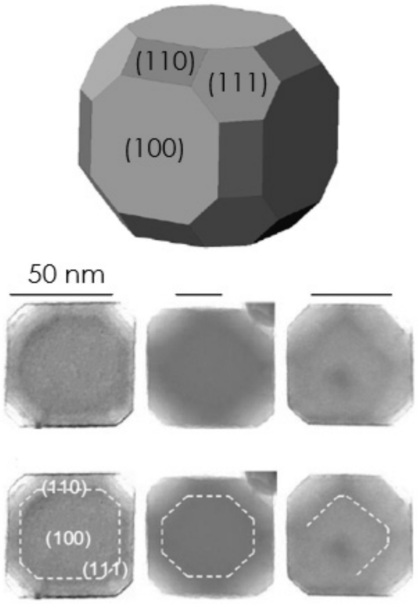

Figure 1. Top: scheme of a cubic MgO nanoparticle (NP) during dissolution in H_2O: (110) and (111) facets emerge on the initially (100) limited NP - Bottom: TEM images of MgO NPs which show an increasing importance of (111) facets as dissolution proceeds.[6]

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Notes

(O2-S1)

CONTROLLING DEFECTS IN ZnO SURFACE

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ABSTRACT

With its outstanding chemical and physical properties, ZnO encompasses an amazing spectrum of applications competing, thus, to be one of the most promising compounds among other functional materials. The presence of very rich defect chemistry – with Zn interstitials and oxygen vacancies known to be the predominant ionic defect types [1, 2] – complicates, however, the advances necessary for ZnO to become a front-runner in the context of new applications. Only to precise which defect dominates in native, undoped ZnO is still a matter of great controversy.

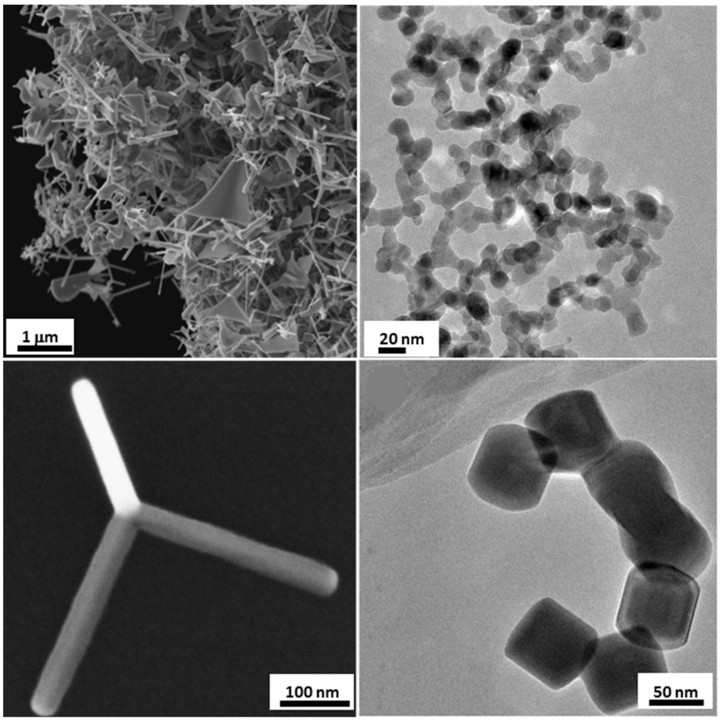

Figure 1: TEM images of ZnO nanoparticles obtained via metal combustion (left) and chemical vapour synthesis (right).

Our goal was to establish the relationship between, synthesis, processing, and defects' chemistry of ZnO nanoparticles. For this purpose ZnO nanopowders – different in terms of defects – were fabricated via two evaporation techniques (Fig.1) and characterized under various ambient conditions by combining Raman, Photoluminescence, Infrared and Electron Paramagnetic Resonance spectroscopies. In this contribution, we will show that the nature and concentration of defects in ZnO – both, in the bulk and at the surface – can be: (i) controlled by the judicious choice of synthesis and processing parameters and (ii) can be identified on the basis of their interaction with water and/ or hydrogen via combination of complementary spectroscopic techniques [3].

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Notes

(O3-S1)

SYNTHESIS OF TiO_2 NANOPARTICLES WITH CONTROLLED CHARACTERISTICS BY SOL-GEL TECHNOLOGY

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ABSTRACT

It is well known that the effectiveness of titania as a photocatalyst is very sensitive to its crystal phase, particle size and specific surface area [1]. A good crystallinity is often required to reduce the formation of electron traps, which might affect the photocatalytic efficiency, and a large specific surface area can supply more active sites and higher number of adsorbed substrates. To obtain highly active TiO_2 photocatalysts, therefore, it is important to maximize simultaneously these two properties. However, the synthesis of stable titania with high crystallinity, large surface area and small size is still a challenge [2].

Among three crystalline phases of TiO_2, anatase exhibits the highest photocatalytic activity. Traditionally, crystallinity of TiO_2 has been developed by calcinations (anatase requires calcinations at minimum 350 ºC during 12 h), which frequently results in partial or total collapse of mesoporous structure [3]. The use of high temperatures would result in the growth of crystal particles, causing structural collapse and, therefore, decrease in the specific surface area of TiO_2. Therefore, the development of mild temperature synthesis of nanocrystalline titania is essential for its wider range of applications [4].

There are many low temperature methods available for the synthesis of TiO_2 nanoparticles, such as ultrasonic irradiation, UV light assistance, solvent evaporation-induced crystallization, sol–gel and so on. Among these methods, the sol–gel method is the most widely employed due to the inexpensive equipment required, the low temperatures used and the homogeneous and highly pure product produced [5]. In addition, the use of a microemulsion as starting point in the sol-gel process for the TiO_2 synthesis allows the control of the nanoparticles specific size and morphology.

In the current work, the influence of the main parameters of the synthesis was studied: nature of surfactants, water-surfactant-oil ratio, co-surfactant and calcination time and temperature. The prepared TiO_2 nanoparticles present different sizes, crystallinity degrees and surface areas depending on the experimental conditions used. The understanding of the influence of each parameter of the process on the final properties of the TiO_2 nanoparticles along with the flexibility of the synthesis method allow to tune the nanoparticles properties on demand, as a function of the specific application.

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Notes

(O4-S1)

MODELLING THE DISCONTINUOUS TiO_2 ANATASE CRYSTALS' GROWTH IN HYDROTHERMAL SYNTHESYS

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ABSTRACT

The TiO_2 nanoparticles crystallization from solutions containing Ti precursor as $Ti(TEOA)_2$, in hydrothermal conditions, is modeled considering the chemical reactions that occur in the liquid phase and generate the solvated TiO2 together with the crystal nucleation and growth until final product characteristics are reached. The crystal growth model is based upon the series of papers by Fichthorn and co-workers [1-3] devoted to the structure and growth of anatase crystals. The growing mechanism is the "oriented attachment", according to which two discrete events are considered:

- the attachment along an energetically favorable facet of two distinct crystals
- the rearrangement of the parents into a newborn crystal (when a deficit of molecules appears, it is compensated by harvesting them from the solution).

The chemical reactions considered are mainly represented by the stepwise decomposition of Ti hydroxides resulted from the $Ti(TEOA)_2$ hydrolysis, and the generation of TiO_2 that nucleates from the solution. The mathematical model captures both the continuous variation of chemical species in the liquid phase and the discrete growth of the crystals which define the crystal size distribution (CSD).

In the present work, it is postulated that no matter how big the crystal is, it has a central square layer, which can be seen as a symmetry plane between two mirrored square frusta building a truncated square pyramid. The crystal growth is realized by the collision of two parent particles. An important hypothesis related to the growth of is related to the number of molecules needed by the resulted crystal: if the resulting crystal is formed by more molecules than both parents, during aggregation, the deficit is covered harvesting the necessary supplemental molecules from solution.

The discrete events that can occur during crystallization are selected considering a greater probability to collide for crystal with close masses. Collisions that result in crystals with two high deficits to be compensated from the solution or with negative deficit that would be resolved by solvation are disregarded, considering that these cases are unfavorable energetically.

By solving the kinetic and growth model, the variation of species liquid concentrations and the dynamics of CSD are obtained. The final CSD was obtained starting from a solution with 65 mM $Ti(TEOA)_2$ concentration, supplemented by TEOA 40 mM, at pH=10 and 170 °C. The CSD mode is at 17.5 nm and the size range is 14-21 nm which is in good agreement with experimental measurements.

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Notes

(O5-S1)

EXPERIMENTAL APPROACHES AND PARADIGMS FOR SHAPE CONTROLLED SYNTHESYS OF TiO_2 NANOPARTICLES

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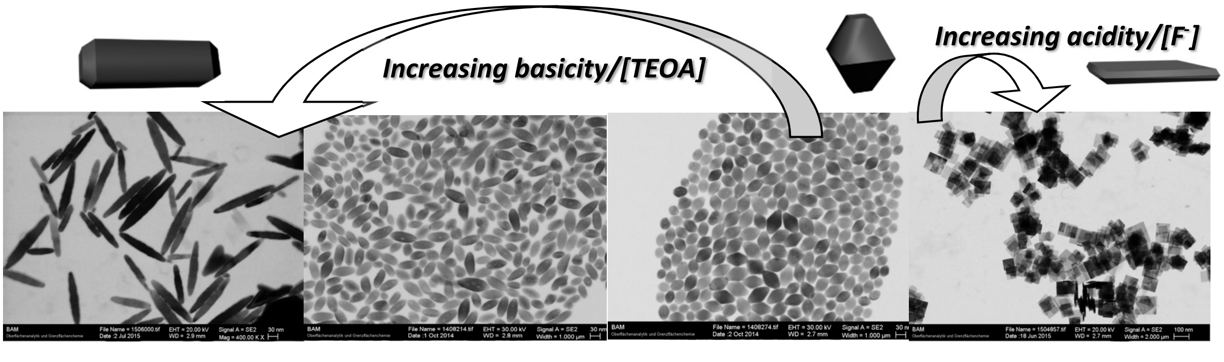
ABSTRACT

Titanium dioxide is one of the most studied metal oxides due to its interesting chemical, surface, electronic and (photo)catalytic properties. These properties provide this material of multisectorial applications, ranging from healthcare, photocatalysis, smart materials with self cleaning and self sterilizing properties and solar energy harvesting (photovoltaics and water photosplitting). However it is difficult to correlate the functional properties of TiO_2 nanomaterials to the properties at single nanoparticle level due to the high polydispersity in shape, size and surface properties of the currently available TiO_2 nanoparticles (NPs) Although intensive experimental and theoretical studies have been conducted on the reactivity of different surfaces of metal oxides such as TiO_2 [1,2] much less attention is paid on the dependence of functional properties, like photocatalytic activity, dye adsorption, open circuit potential and fill factor in dye sensitized solar cells, on crystal facets in different orientations [3]. One of the goal of SETNanoMetro is the development of design rules to tune crystal facets of TiO_2 NPs in order to optimize and control functional properties. By tuning the ratio of different facets, the functional properties would be correspondingly changed. In the present work we have developed a series of design rules in order to obtain sets of anatase TiO_2 NPs with low polydispersity and to tune their shape and their size though hydrothermal processing of Ti(IV)-Triethanolamine complex in presence of different shape controllers (OH-, triethanolamine, fluoride). Through a careful experimental design the influence of many process parameters (pH, temperature, shape controller type and concentration) on the synthesis outcome (size, shape and polydispersity), a predictive soft model was developed. The model is able to predict reasonably well the synthesis outcome allowing to tune the shape factor from 5 (prisms) to 1.5 (bipyramids) to 0.2 (platelets). This allows to control the main crystal facets exposed ranging from (100) to (001).



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Notes

(O6-S1)

OXYDATION ROUTE DETERMINES THE MAGNETIC AND RELAXIVITY PROPERTIES OF IRON OXIDE NANOCRYSTALS: TOWARD HIGHLY EFFICIENT MRI CONTRAST AGENT

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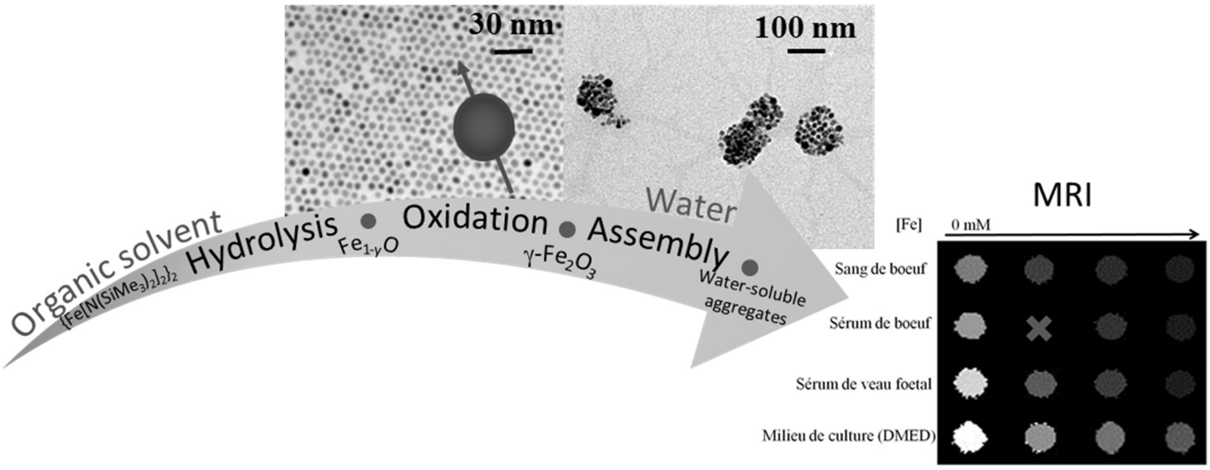
ABSTRACT

The synthesis of ultrasmall superparamagnetic iron oxide nanocrystals (USPIO) with controlled size distribution and crystallinity has been a constant challenge for advanced applications such as MRI or hyperthermia, which require specific magnetic features.[1-3] Using an organometallic approach, we investigate independently the hydrolysis and oxidation steps in the synthesis of USPIO. The USPIO were investigated by a variety of analytical techniques and we demonstrate that the oxidation route influences the structural and magnetic properties of the USPIO. In particular, the property most directly related to the efficiency of MRI contrast agents, the magnetic relaxivity, appears to depend critically on the elaboration process. Thus, starting from highly homogeneous wüstite ($Fe_{1-\gamma}O$) Ncs, the selection of the oxidation pathway led to maghemite (γ-Fe_2O_3) Ncs optimized for MRI. Finally, the USPIO are assembled into SPIO (superparamagnetic iron oxide) aggregates of ca 150 nm, which are water dispersable and exhibit relaxivity values ca 4 time higher than the commercial Feridex® MRI contrast agent. Such SPIO aggregates are moreover stable in a lot of different physiological media (beef blood, beef serum, foetal calf serum, DMED cell culture). These SPIO aggregates consequently exhibit a significant decrease of the signal even with a very short echo time of 8 ms which is of paramount importance in clinical trials because it significantly decreases the duration of the MRI measurement and can significantly improve the patient's well-being.[4]



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Notes

(O7-S1)

ISOMORPHIC SUBSTITUTION VERSUS OXIDE NANOCLUSTERS FORMATION IN IRON-DOPED ALUMINO-SILICATE NANOTUBES OF THE IMOGOLITE TYPE

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ABSTRACT

Imogolite (IMO) is a naturally occurring material with chemical formula $(OH)_3Al_2O_3SiOH$ forming nanotubes (NTs) with an external surface made by Al-O-Al and Al(OH)Al groups and an inner surface lined by silanols.[1,2] The outer surface has an amphoteric nature, whereas the inner one is extremely hydrophilic. Several means of surface modification of IMO NTs have been proposed, so far, but only a few papers deal with the isomorphic substitution of Al^{3+} with Fe^{3+}, that gives rise to a material of the type $(OH)_3Al_{2-x}Fe_xO_3SiOH$. On the one hand, doping of iron could modify the conduction and magnetic properties of the material (IMO is an insulator and a diamagnetic material); on the other hand, formation of Fe(OH)Al groups at the outer surface of NTs modifies its physico-chemical and catalytic properties.

In this work, the textural and surface properties are reported of Fe-doped aluminosilicate nanotubes (NTs) of the imogolite type, IMO, with formula $(OH)_3Al_2$-xFexO$_3$SiOH (x = 0, 0.025, 0.05). Samples were obtained by either direct synthesis (Fe-x-IMO) or post synthesis loading (Fe-L-IMO), with 1.4 wt % Fe (both Fe-0.05-IMO and Fe-L-IMO) or 0.7 wt% Fe (Fe-0.025-IMO). Their textural properties were characterized by High-Resolution Transmission Electron Microscopy (HR-TEM), X-rays Diffraction from powders (XRD) and N_2 isotherms at -196 °C. The effects of the presence of (different) iron species were studied, *inter alia*, by UV-Vis and Electron Paramagnetic Resonance (EPR) spectroscopies. The surface properties were characterized by IR spectroscopy and z-potential measurement.

Fe^{3+}/Al^{3+} isomorphic substitution was found to be the main process occurring by direct synthesis, with Fe^{3+} ions substituting for octahedral Al^{3+} ions located at the external surface of NTs, giving rise to isolated high-spin Fe^{3+} sites.

By post-synthesis loading, preferentially formation of Fe_2O_3 nanoclusters occurs, likely due to the natural tendency of iron to form Fe-O-Fe bridges: some isomorphic substitution, however, also takes place, opening the possibility to exchange Al^{3+} ions in pre-formed IMO NTs, a simpler procedure with respect to direct synthesis.

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Notes

Session 2 (S2)

Preparation and characterization of nanostructured films

(KN-S2)

DESIGN OF NANOSTRUCTURED TITANIA THIN AND THICK COATINGS THROUGH COLLOIDAL PROCESSING

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ABSTRACT

Colloidal processing has demonstrated to be an efficient approach for the manufacture of complex-shaped ceramics, as well as for the production of laminates, substrates and coatings [1,2]. The accurate control of the interparticle forces operating in the bulk of a suspension allows maintaining the stability along the different stages of the processing schedule and thus, reducing the tendency to agglomeration. Colloidal processing is well established for the manufacture of bulk materials with complex geometry and/or tailored microstructures, such as in the case of multilaminates and functionally graded materials. However, the principles of colloidal processing can be also applied successfully in the production of either thin or thick films through a variety of techniques in which the preparation of stable suspensions of nanoparticles are a major concern.

In the present work the main issues concerning the stability of nanopowders in water are described, focusing on the mechanisms of colloidal stability and the rheology of concentrated suspensions. In most cases, commercial colloidal suspensions are being used to produce nanostructured films and coatings, but very few compositions are commercially available and their solids contents are relatively low for the production of thick coatings. One feasible procedure to concentrate those commercial suspensions of nanoparticles is to use them as a dispersing medium for other powders, thus allowing increasing by 2-3 times the original solids loading of the dispersion [3]. Moreover, those suspensions can be used in different technologies, from those commonly used in the preparation of thin films such as dipping and electrophoretic deposition [4] to the production of porous, thick coatings by plasma spraying techniques [5] .

The present work describes the processing parameters involved in both the synthesis and the stabilization of titania nanoparticles for the production of nanostructured coatings, demonstrating the increased reliability and enhanced properties achieved after an adequate control of the colloid chemistry and the rheology of the suspensions. Different nanosized titania materials are studied and compared, including powders and colloidal suspensions, as well as their mixtures. The preparation of stable, concentrated suspensions of titania nanopowders is studied in terms of zeta potential measurements as a function of pH, type and concentration of polyelectrolytes, mixing time using an ultrasounds probe, etc. The preparation and rheological properties of concentrated suspensions is also reported. Finally, examples of the influence of the processing parameters on the properties of coatings produced by dipping, electrophoretic deposition and plasma spraying are given.

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Notes

(O1-S2)

SYNTHESIS OF HYBRID ACRYLIC/TiO_2 FILMS AND THEIR USE IN BACTERIAL AND POLLUTANT DEGRADATION

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ABSTRACT

Since the industrial revolution, photocatalytic materials have known an increasing interest due to their high efficiency in decontaminating air and wastewater as well as their good self-cleaning and antibacterial properties.[1-2] Among all the photocatalysts, TiO_2 presents high photoactivity, low cost, low toxicity and good chemical and thermal stability which make it the photocatalyst of choice for most applications.[3] In many applications, in order to be used efficiently, TiO_2 nanoparticles should be incorporated into polymeric matrices (substrates) or suspended in a dispersion provided that they can be recovered and reused. Therefore, it is interesting to develop a technology platform that allows the production of hybrid polymer latexes that are film forming and/or can be used as prepared that contain the photoactive material and other functionalities that might be required (magnetic properties). Thus a technology that permits a tight control of the morphology of composite particles is needed. Miniemulsion polymerization has demonstrated to fulfill these requirements.[4] For the application considered in this work, the TiO_2 should be located at the surface of the hybrid polymer particles in order to be accessible after film formation.[5] Therefore, in this work TiO_2 Pickering stabilized latexes were synthesized by miniemulsion polymerization. The effect of the TiO_2 content on the hybrid particle size as well as the film morphology was studied by TEM and AFM techniques. It was found that the particle size was controlled by the amount of TiO_2 used as stabilizer; the larger the concentration of TiO_2, the smaller the particle size. Also, the films presented perfect honey comb structures (see TEM and SEM images) and the higher was the TiO_2 content, the higher was the thickness of the TiO_2 walls between particles. Finally, it was observed that TiO_2 was present at both sides of the film, its concentration being larger at the film-air interface than at the film-substrate interface. The photocatalytic and antibacterial activities of films with different TiO_2 concentrations were measured. It was found that all the films showed excellent self-cleaning activity and that the photocatalytic activity index was little affected by the concentration of TiO_2 and the roughness of the film. On the other hand, the antibacterial activity was greatly affected by the roughness of the film and the film with the lowest TiO_2 concentration presented the best properties. As an example, Figure 1 presents an overview of the results obtained for a sample containing 10 wbm % TiO_2; from left to right: a TEM micrograph of the Pickering latex dispersion, a TEM and SEM micrograph of the cross-section of the film obtained by casting the latex and the resulting photocatalytic and antibacterial activities obtained.

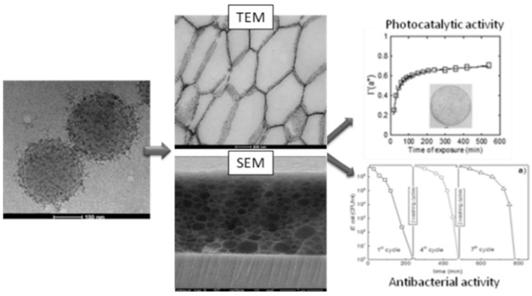

Figure1. Results of all the analyses carried out on the sample containing 10 wbm %

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Notes

(O2-S2)

PHOTON-DRIVEN SELF-ORGANIZED GROWTH OF METALLIC NANOPARTICLES IN TiO₂ FILMS

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ABSTRACT

Exciting the plasmon resonance of silver nanoparticles (NPs) embedded in a TiO_2 thin film with a visible laser scanning the film surface can give rise to an interesting self-organization process (Fig. 1a-b) [1]. The latter leads to the generation of waveguiding metallic photonic crystals made of periodic nanoparticle arrays buried in the film, which exhibit singular optical properties (Fig1c) [2]. Their generation is a complex process involving various physico-chemical mechanisms, which are shown to be driven by both radiative and non-radiative decays of the localized surface plasmon resonance of Ag NPs. Charge transfers from metallic NPs to the semiconductor TiO_2 matrix, through the Schottky junction, and the material heating result in two opposite effects that are the shrinkage or the growth of silver nanoparticles through oxidation or reduction/growth reactions, respectively. We will demonstrate how the intensity distribution of the laser beam scanning the sample at a constant speed determines the relative weight of these reactions during exposure and how their competition influences the final size of silver nanoparticles [3]. Moreover, the parameters of the self-organized photonic crystals are driven through scattering by plasmonic nanoparticles i.e. through the radiative decay of the plasmon. The latter is shown to excite a guided mode of the TiO_2 film, whose interference with the incident field is shown to directly influence the period and the orientation of nanostructures.

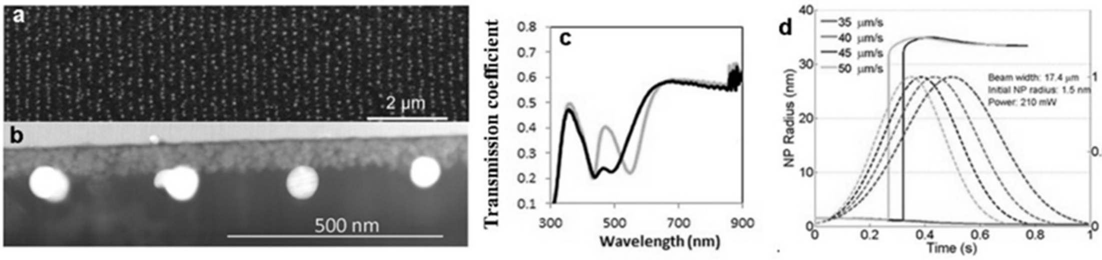

Figure 1: SEM top view (a) and cross-section (b) of a self-organized waveguiding metallic photonic crystal. (c) Transmission coefficient for cross-polarizations. (d) Simulated changes in the nanoparticle size during laser scanning for various scanning speeds.

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Notes

(O3-S2)

SILICON NANOWIRES FABRICATION BY SUPRAMOLECULAR SELF-ASSEMBLY AND METAL ASSISTED CATALYTHIC ETCHING

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ABSTRACT

Silicon nanowires (SiNWs) have witnessed an increased interest in recent years, due to good scalability and their electric and thermoelectric properties. A proposed method presenting noticeable advantages in term of cost, size control (section shape, dimensions) and typology (doping level and type) is Metal-Assisted Chemical Etching [1]. MACE can be used both in presence of a quasi-continuous metal film or a patterned one, in our case by nanosphere lithography. This yields to ordered arrays of nanowires with diameter defined by the initial spheres sizes.

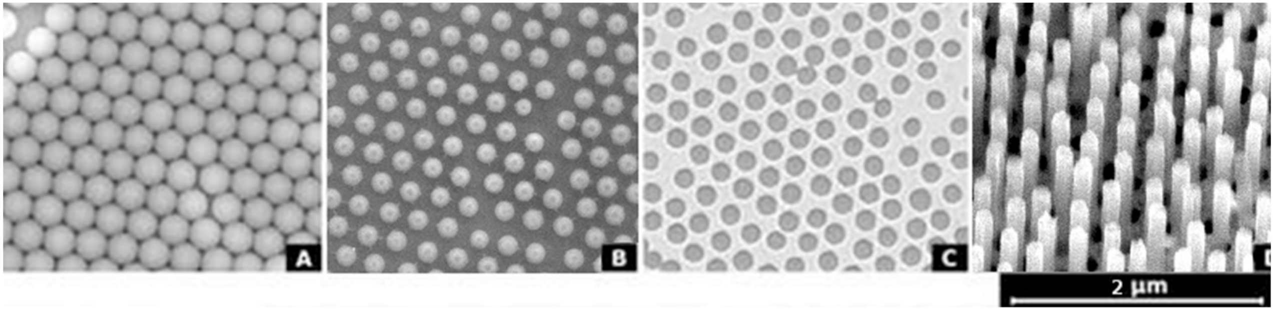

Figure 1 SEM images, Si NWs fabrication steps: A) Polystyrene nanospheres are spread on the silicon substrate by spin-coating; B) Reduced nanospheres after O_2 plasma etching; C) Metal "antidot" pattern after nanospheres ablation; D) Obtained SiNWs after 1 min etch.

These arrays of SiNWs are promising for the realisation of high performance nanostructured anodes for solid state batteries, for gas and bio sensing and for nanoelectronics.

Polystyrene nanoparticles were synthesized by emulsion polymerization. The polymerization reactions were carried out in a 1 L five-neck equipped with a condenser, a mechanical stirrer, a thermometer and inlets for nitrogen and styrene. The polystyrene nanoparticle size was determined by scanning electron microscopy and it was 179 ± 7 nm. The polystyrene nanospheres were then spread on highly p-doped Silicon 10-20 mΩ·cm <100> substrates by spin-coating, in order to obtain self-assembled monolayer arranged into hexagonal closed packed structure. A portion of a silicon substrate covered by the monolayer can be seen in figure 1A. Oxygen plasma etching was performed in order to reduce their dimension down to 120 ÷ 130 nm. At this stage, a 20 nm thick gold film was deposited on the sample using an e-beam evaporator. A so-called "antidot" metal pattern remained on the silicon surface after spheres removal in ultrasonic bath, Figure 1B and 1C. MACE was performed dipping the sample in the chemical solution composed of deionized water, hydrogen peroxide and hydrofluoric acid (H_2O:H_2O_2:HF 1:1:3) heated at 60° C [2]. An ordered array of well-defined Si nanowires is finally obtained, as shown in Figure 1D. A complete characterisation study of these nanowires including TEM, electrical and thermal conductivity measurements is in progress.

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Notes

(O4-S2)

DETERMINATION OF THIN FILM POROSITY BY SEM/EDX: APPLICATION TO MESOPOROUS TiO_2 LAYERS

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ABSTRACT

Various applications such as automotive catalysts, photocatalysis and sensors rely on thin coatings with high active surface area. The development of new and improved coatings requires in-depth understanding of the film morphology and texture. Especially the film porosity is a key parameter to identify structure-property relationships in applications. However, an accurate porosity determination of thin porous coatings is a challenging. In this contribution we present and discuss a new approach for determining the porosity of films by X-rays at SEM.

The mass coverage of layers can be calculated by the film analysis software STRATAGem[1] from EDX determined *k*-values based on the well known Pouchou and Pichoir approach.[2] We present an approach for determination of the porosity by a combined SEM/EDX/STRATAGem analysis. From the STRATAGem-derived mass coverage and the coating thickness as determined by cross-section SEM micrographs, the average density of the film can be obtained. In a second step, the porosity is calculated from the measured porous film density and the literature value for the pore walls bulk density. The complete approach is sketched in Figure 1.

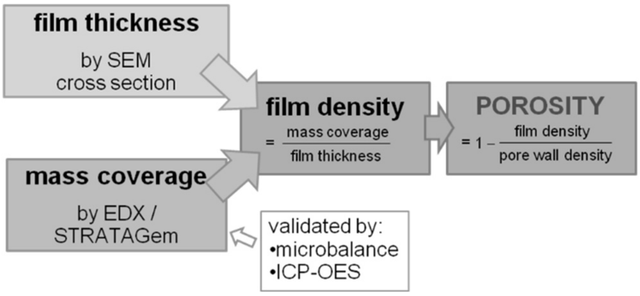

Figure 1: Illustration of the approach for the determination of the porosity of thin films by EDX/SEM analysis

The general procedure to determine the porosity is demonstrated on thin mesoporous TiO_2 films on Si wafer substrates. The TiO_2 films were synthesized by a template-assisted synthesis route, which provides a scalable model system with tunable porosity.[3] EDX spectra of these films were measured at different beam voltages by using a high-throughput SDD EDS detector which enables a time-efficient analysis. From the measured *k*-values for Ti K⍰ and Si K⍰ in dependence on the applied beam voltage, STRATAGem calculated the mass coverage. An excellent agreement was obtained between the mass coverage calculated by STRATAGem and the mass coverage determined by weighing and ICP-OES of the same film. The increasing porosity of thin TiO_2 films illustrated in Figure 2 could be calculated quantitatively by the new approach. These combined SEM/EDX/STRATAGem analyses demonstrate a unique tool for non-destructive examination of the porosity of thin porous films.

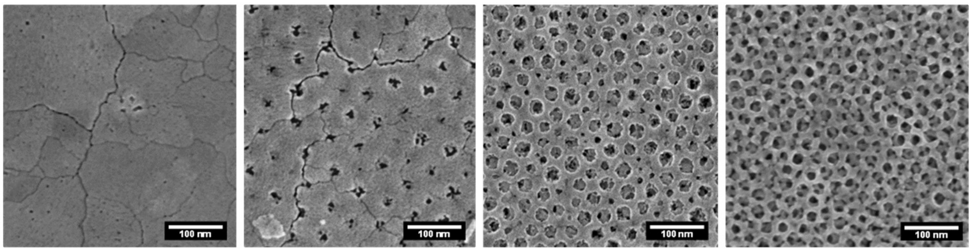

Figure 2: Top-view SEM micrographs of TiO_2 films with increasing void fraction, i.e. film porosity from left to right.

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Notes

(O5-S2)

MESOSCALE MODELLING OF THE STRESS-STRAIN AND SLIDING BEHAVIOR OF A POLYMER MATRIX COMPOSITE BASED ON EPOXY AND 6 VOL% SILICA NANOPARTICLES

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ABSTRACT

Polymer matrix composites (PMCs) with nano-scale inorganic fillers are attracting more and more interest of material engineers because they offer the opportunity of tuning material properties in a wide range [1]. During our own previous work the beneficial role of silica nanoparticles on friction and wear reduction of an epoxy-based PMC was observed experimentally [2, 3].

A model based on movable cellular automata (MCA) is described and applied for simulating the stress-strain and sliding behavior of a nanocomposite consisting of an epoxy matrix and 6 vol% of homogeneously distributed silica nanoparticles.

Tensile tests were used for verification of the model. It was realized that a slight modification of epoxy properties due to the addition of silica nanoparticles had to be taken into account in order to obtain good correlation between experimental and modelling results. On the other hand, sliding simulations revealed no susceptibility of results to slight modifications of matrix properties, but a significant impact of nanoparticles on the interface structure and smoothness of sliding mechanism.

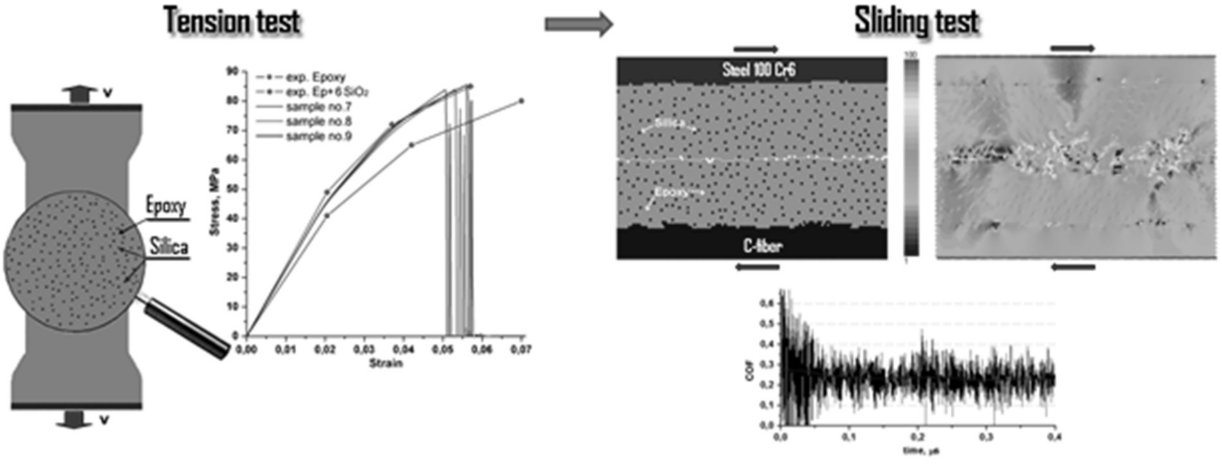

Figure 1. Simulated stress-strain curves (samples 7-9) compared to tensile test data of pure epoxy and epoxy filled with silica nanoparticles (left), and modelling setup, strain intensity map and friction evolution during sliding simulation (right)

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Notes

Session 3 (S3)

Characterization and metrology of nanoparticles

(KN-S3)

METROLOGY ON THE NANO SCALE: PRINCIPLES AND CHALLENGES

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ABSTRACT

After a short introduction into metrological principles and hierarchies, the latter mainly applicable to legal metrology, the paper will focus on ways to disseminate comparability of measurement results, namely

- the system of (accredited) calibration services
- reference materials
- inter-laboratory comparisons.

Reference materials play a key role in external quality assurance of calibration and testing laboratories. While calibration laboratories will normally take their proof of accuracy and the establishment of traceability from the National Metrology Institute (NMI), testing laboratories with their ultra-broad spectra of investigated measurands may, for the establishment of the same performance characteristics, either refer to inter-laboratory comparisons (where existing) or to reference materials (RM), in particular those coming with a certificate.

The paper will briefly mention different uses of (certified) reference materials including proof of precision, proof of accuracy, validation of (new) methods, and calibration of testing methods, and emphasise its role in disseminating traceability of measurement results [1].

Special attention is given to reliable estimation of measurement uncertainty as a key issue in assuring comparability and compatibility of results, and in particular in establishing traceability to a common reference, be this the International System of Units (SI) or any other developed system of references [2].

Peculiarities and challenges of the approach with respect to the specific needs of measurements on the nano scale will be discussed, namely the (most often) multivariate character of measurands, and the strong model dependence of results.

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Notes

(O1-S3)

A “RAMAN CALIPER” FOR SIZE CHARACTERIZATION OF TiO_2 NANOPARTICLES: EXPLOITATION OF PHONON-CONFINEMENT EFFECTS ON RAMAN SPECTRA

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ABSTRACT

Nanostructured titanium dioxide is one of the most studied oxide semiconductor systems with a variety of technological applications. The possibility of tailoring its properties via the control of the particle size (in titanium oxide nanopowders), or via the nanostructure in thin films, has opened perspectives for improved applications of this versatile material. Moreover, the possibility of controlling the crystalline phase adds a degree of freedom in the engineering of tailored structures. The most abundant crystalline phase of TiO_2 are anatase and rutile. Titanium oxide in the anatase phase has long been known to possess properties which render it interesting for applications in photovoltaic cells, photoactivated catalytic processes, gas sensors, and functional surfaces.

The use of nanostructured titania on a large scale relies on several conditions that are difficult to obtain at the same time. Nanoparticle mass production methods must provide the possibility of independently control size distribution (aiming at a narrow size dispersion), crystalline phase and stoichiometry. Another crucial requirement to be considered for large scale production and application of nanostructured titania is the possibility of characterizing the above mentioned parameters with simple, reliable, and economically sustainable characterization methods.

Raman spectroscopy is a very strong candidate to be the technique of choice for characterization of titania nanopowder. Anatase has tetragonal structure with two formulas per unit cell and thus shows well distinct Raman fingerprint, with six Raman active modes ($A_{1g} + 2B_{1g} + 3E_g$). The low-frequency E_g mode (143 cm^{-1}) shows a strong dependence on the sample nanostructure: in particular, with decreasing the nanoparticle size, the peak at 143 cm^{-1} blueshifts and asymmetrically broadens with a high-frequency shoulder. This can be attributed to phonon-confinement effects. [1,2]

The phonon-confinement is involved in the breakdown of the phonon momentum selection rule: thanks to Heisenberg uncertainty relations, $q \neq 0$ phonons can be Raman active and the phonons from the whole Brillouin zone will contribute to Raman scattering. The weight of the the off-centre phonons increase as the grain size decreases: the phonon dispersion causes an asymmetric broadening and the shift of the Raman peak. The trend of both effects versus the nanoparticle size can be predicted theoretically, through a method well-described by Campbell and Fauchet [3,4]. In this work, performed in the framework of SETNanoMetro project on metrological characterized TiO_2 NPs, we will show the results on evaluation of particle size by Raman spectroscopy and theoretical model on optical phonon-confinement in NPs. [5-8]

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Notes

(O2-S3)

SHAPE RECOGNITION OF NANOPARTICLES BY HIGH-RESOLUTION SEM AND TSEM

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ABSTRACT

Engineered nanoparticles (NPs) are used as an active material in sensors, photovoltaics, photocatalysis, etc. Numerous publications have shown that particular facets of NPs dramatically influence their performance, e.g. in photocatalytic reactions with TiO_2 NPs [1, 2]. Therefore, information about the NP morphology expressed as area ratios of particular facets is highly demanded for the development of advanced nanomaterials.

The determination of the particle size distribution for spherical NPs is a task resolved rather easily by various techniques. However, measuring the morphology of individual NPs having complex 3D geometries like cubes, prisms or (bi)pyramids is challenging. Often, only time-consuming TEM and TEM-tomography experiments can resolve the 3D structure and facets of particles in the nanometer range accurately. We present new approaches based on i) top-view high resolution SEM and ii) in-depth view, transmission SEM (TSEM) for the determination of the full shape of facet-controlled NPs.

From top-view high resolution SEM (approach i) we could identify the 3D geometry and the individual facet boundaries of NPs. A computer-generated 3D skeleton was manually matched to these facet boundaries, thereby yielding the necessary parameters for a full 3D description of the NP shape. The evaluation of the NP shape from TSEM (approach ii) relies on an automatic image analysis: The 2D projection of the particles on the image plane depends strongly on their orientation with respect to the incident electron beam. Taking only those particles into account for which the 2D projection coincides with an assumed silhouette for standing or lying NPs on the substrate, the size of the corresponding NP facet can be determined. Due to automated image analysis, statistically relevant amounts of data could be generated quickly and lead to reliable estimates of the NPs facet size.

These general procedures to determine the NP shape is demonstrated on truncated bipyramidal TiO_2 anatase NPs. The TiO_2 NPs were synthesized by a ligand-assisted synthesis route, which provides a scalable model system with tuneable TiO_2 NP geometries [1, 2]. Figure 1 presents top-view SEM micrographs of TiO_2 anatase NPs. The truncated bipyramidal shape is clearly recognizable in Figure 1A. An enlarged part of A shows a single NP where individual facet boundaries can be identified (Figure 1B). A computer-generated 3D skeleton was matched to the facet boundaries (Figure 1C) which results in a full 3D description of the NP shape (Figure 1D). The corresponding NPs lengths and widths could also be measured from the TSEM micrograph.

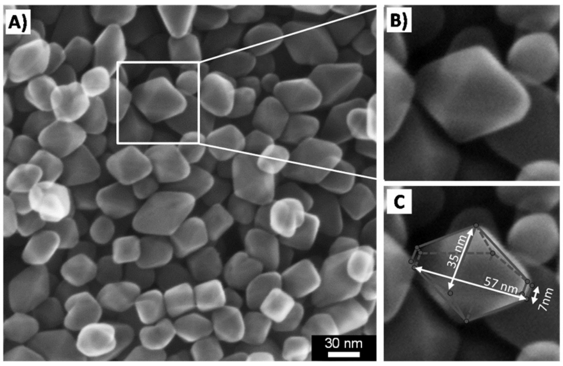

Figure1. Top-view SEM micrographs of truncated bipyramidal TiO_2 NPs, A) overview, B) zoom-in on a single NP, C) generated 3D skeleton matched to facet boundaries.

In order to validate the new methods and estimate the associated measurement uncertainties, TSEM images of randomly oriented bipyramidal particles with known dimensions were simulated and evaluated in the same way as the measured images. A good agreement was obtained between the known parameters and the evaluation results. Furthermore, for selected NPs, the obtained dimensions were confirmed by HRTEM/SAED measurements.

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Notes

(O3-S3)

SURFACE STRUCTURE OF TiO2 NANOPARTICLES WITH ENGINEERED MORPHOLOGY: INVESTIGATION AT MOLECULAR RESOLUTION

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ABSTRACT

Refinement of the synthetic procedures by accurate control of the experimental parameters and the use of shape controllers during the synthesis allow nowadays the fabrication of nanostructured materials engineered to meet specific needs in a variety of technological applications. In the case of TiO_2, the solid studied here, these cover a wide area ranging from photocatalysis and photovoltaic to health.

For some applications, like the production of films, a main requirement can be the control of the nanoparticles morphology, *i.e.* of their shape and size. Shape controlling molecules added during synthesis can effectively address the growth of the nanoparticles along some preferential crystallographic directions. The effect of the shape controller can be monitored in this case by scanning or transmission electron microscopies.

Possible effects of the shape controller on the fine structure of the faces terminating the nanoparticles, in terms of induction of structural defects, of surface reconstruction processes, etc. are on the contrary more difficult to be revealed as they occur at the atomic scale. In this respect, it is worth underlining that the *real* structure of the exposed surfaces can be of paramount importance for all those processes where the behavior of the nanoparticles is determined by a chemical interaction with surrounding molecules (as is the case in adsorption, sensing, catalysis and photocatalysis, biocompatibility/toxicity, etc.). At this level surface characterization by microscopy techniques is less effective either because they do not reach sufficient spatial resolution (as for SEM and conventional TEM), or because despite a good resolution (as for HR-TEM) they do not allow a statistically representative evaluation of defective structures which can involve limited portions of the nanoparticles and/or be randomly distributed.

We show in this paper that the detailed study of the fine surface structure of solids like TiO_2 nanoparticles with different aspect ratio is made possible by infrared spectroscopy of adsorbed molecular probes (CO), possibly supported by HRTEM data and *ab initio* theoretical modeling. By this technique the nature of the exposed sites (mainly the Lewis acidic centers constituted by the coordinatively unsaturated cations) can be inferred from the shift of the vibrational frequency induced upon polarization by physical adsorption of the probe molecule with respect to the free state. The relative concentration of different surface sites can be also evaluated by comparison of the intensity of the associated bands.

Notes

(O4-S3)

EVALUATION AND COMPARISON OF PARTICLE SIZING TECHNIQUES WITHIN THE EC/FP7 PROJECT NANODEFINE

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ABSTRACT

The NanoDefine project [1] has the aim of providing help for the implementation of the EC definition of a nanomaterial [2]. This task is a metrological challenge as the definition requires the evaluation of the smallest particle dimension median in number metrics, within the size range from 1 nm to 10 µm. Most of the available particle sizing techniques do not cover the full required size range and consequently, a suitable, material dependent combination of methods needs to be found. Furthermore, depending on the method, the resulting particle size distributions can be number-, mass-, or intensity-weighted, requiring a valid and reliable conversion into the number metrics required by the EC definition.

To develop a robust, cost-efficient and reliable procedure for the decision process, the available particle sizing methodologies are evaluated on a broad range of materials in the form of powders, covering different particle shapes and chemical compositions, including possible surface coatings of the particles, in a so-called real world performance testing. Furthermore, consumer products of practical relevance containing nanoparticles are also taken into account.

Suitable sample preparation protocols are developed. According to well defined performance criteria, methods are selected for further improvement. Suitable nano reference materials are used as calibrants. The experience gained during this process will be made publicly available in the form of a methods manual and a web-based etool, which guides a non expert through the decision process whether to consider a given material as nano or non-nano according to the EC definition.

To ensure the persistence of the project outcome beyond the project duration, the developed procedures are going to be submitted as proposals to standardization bodies (ISO, CEN, DIN).

Within this contribution, an overview about the NanoDefine project will be given and first results of the real world performance testing of state of the art characterization techniques on the unique set of NanoDefine real world materials are going to be presented. From these results, first conclusions about the material dependent ranges of applicability for the considered particle sizing techniques can be drawn. The method specific advantages as well as the analytical challenges encountered will be highlighted.

Acknowledgements: The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 604347.

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Notes

(O5-S3)

AUTOMATED ANALYSIS OF NANOPARTICLES BY HIGH-RESOLUTION TRANSMISSION SCANNING ELECTRON MICROSCOPY AND ENERGY DISPERSIVE X-RAY SPECTROSCOPY

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ABSTRACT

Physico-chemical characterization of nanoparticles is a fundamental prerequisite for conducting and assessing (eco)-toxicological tests [1]. Size (size distribution) and chemical composition are only two of the properties which have to be identified in accordance to [2] in order to make (eco)-toxicological measurements reproducible and reliable, hence enabling hazard identification and risk assessment.

To determine particle size distribution as well as elemental composition high-resolution transmission scanning electron microscopy combined with energy dispersive X-ray spectroscopy are appropriate methods. However, problems arise in the low nm range and from polydispersity in size and morphology of the particles within the sample, the size often being smaller than the excitation volume. Size and morphology introduce several effects hindering especially accurate quantitative elemental analysis. There is a lack of validated quantification algorithms and certified reference materials as well as standard operating procedures to be applied to nanomaterials.

In the frame of the European research project NanoValid we are currently investigating the drawbacks and thus the possible improvements which are necessary for quantitative elemental and size analysis. Here, we present examples to elucidate several steps ranging from analysis of e. g. mesoporous silica by automated feature analysis to presentation of results of round robin having the size as measurand.

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Notes

(O6-S3)

DISCLOSING THE STRUCTURAL, STOICHIOMETRIC AND MORPHOLOGICAL FEATURES OF LEAD CHALCOGENIDE QUANTUM DOTS THROUGH X-RAY TOTAL SCATTERING TECHNIQUES

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ABSTRACT

Colloidal lead chalcogenides Quantum Dots (QDs) are an increasingly important class of nanocrystalline materials. Due to strong quantum-size effects, they are very promising materials in solar cells applications [1], photodetectors [2] and thermoelectric devices. [3]

Size-tuneable QDs are usually synthesized using long organic ligands (controlling their growth and preventing them from aggregation) providing metal-rich nanocrystals (NCs). Controlling their structure at the atomic level is the key to fully understanding their peculiar properties and tuning their functionalities. A lot of work has been done on this side, that mainly indicate the formation of non-stoichiometric core-shell NPs, with an excess of Pb atoms at the surface, coordinated by the capping ligands. [4] Also the presence of local Pb disorder has been deeply analysed with several techniques (PDF, [5] EXAFS, [6] MEM [7]) in microcrystalline powders, but it is still strongly debated. Using unconventional Wide-Angle X-ray Total Scattering techniques and a core-shell model relying on the Debye Scattering Equation, we characterized highly monodispersed oleate-capped PbS and PbSe QDs (with nominal sizes in the 3-8 nm range) in colloidal suspensions in terms of crystal structure, size, size distribution and stoichiometry. Data were collected at the MS-X04SA beamline of the Swiss Light Source. Structural modelling was performed using the Debussy Program Suite. [8]

By this innovative approach we were able to obtain very unexpected findings about QDs crystal structure, stoichiometry and morphology that could bring new lights on the understanding of their complex functional properties.

These results will be presented in details within this communication.

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Notes

Poster Session
(PS)

(P1-PS)

THE DebUsSy SUITE 2.0: A POWERFUL TOOL FOR CHARACTERIZING NANOSIZED MATERIALS THROUGH THE DEBYE SCATTERING EQUATION

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ABSTRACT

The Debye Scattering Equation (DSE) provides the total (X-ray, Neutron or Electron) scattering pattern of an ensemble of nanoparticles through the distribution of their interatomic distances, without any assumption of periodicity and order [1]. DSE is therefore a powerful approach for quantitatively determining structural and microstructural properties of nanoscaled materials and nanocomposites, at both the atomic and nanometer length scales.

DebUsSy is a suite of programs implementing the DSE for the analysis of powder diffraction data from nanocrystalline, defective and non-periodic objects [2]. It encodes an algorithm making the DSE calculation, in principle very intensive from the computational time point of view, extremely fast and accurate. The Suite has been successfully applied in modeling different kind of nanomaterials (metals, alloys, oxides, bioceramics, molecular drugs, QDs and metal-organic compounds) [3,4,5].

In this contribution, the new 2.0 release of the DebUsSy Suite [6] will be presented. It includes different kinds of optimization algorithms enabling to extract quantitative micro-structural values of mono- or bi-variate log-normal function to deal with the sample-size distribution, size-dependent lattice expansion, atomic site occupation factors and thermal parameters. Disorder of paracrystalline nature can be modeled according to the Welberry's theory [7]. A python-based Graphical User Interface makes easy to run any of the programs within the Suite and to display predefined or customized plots of the results. Additionally, a satellite suite of utilities has been developed for correcting the experimental data from absorption and instrumental effects, and subtracting extra-sample scattering contributions.

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Notes

(P2-PS)

MICROWAVE AND ULTRAVIOLET ASSISTED SOL-GEL SYNTHESIS OF PHOTOCATALYTIC TiO_2 THIN FILM

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ABSTRACT

Titanium dioxide (TiO_2), a novel inorganic function material with wide bandgap, has recently attracted much attention because it is one of the most prominent materials in the area of photocatalysis. There are many routes to synthesize TiO_2 thin films to obtain the optimum size and phase of crystalline TiO_2, including sputtering, chemical vapor deposition (CVD), spray pyrolysis, electrodeposition, self-assembly and sol–gel [1]. Among these methods, the sol–gel process is one of the most appropriate technologies to prepare thin oxide films. The interest in application of sol–gel method is due to several advantages, such as good homogeneity, ease of composition control, large area coatings, low equipment cost and good photocatalytic properties. However, The TiO_2 film synthesized by sol-gel technique is typically sintered at 350-550°C for approximately 30-120 min to achieve crystallization to the anatase phase and good connections between the TiO_2 nanoparticles [2]. This fact represents an important limitation: the substrates for the TiO_2 must be stable at these high temperatures. In this way, polymeric substrates cannot be employed as substrates. Taking into account that polymeric materials have high potential for being used in photocatalytic applications, mainly in the applications related with water disinfection, it would be interesting to achieve photocatalytic films at lower temperatures.

In the current work, different alternatives were employed to achieve photocatalytic TiO_2 thin films at lower temperatures: the addition of nanoparticles to the sol, the use of alternative heating systems (ultraviolet radiation and microwave heating) and the combination of both of them. As a comparison, TiO_2 thin films were synthesized also by thermal curing in an oven for 2 h at 150 ºC (the maximum temperature due to dimensional stability problems in a high number of polymers). The TiO_2 sol was prepared by using titanium tetraisopropoxide, Brij58 as surfactant and acetic acid as complexing agent. When TiO_2 nanoparticles are employed, a concentration of 5 g/l was employed. The morphology, crystallinity and photocatalytic properties of the films have been analyzed. For the photocatalytic analysis, the effect of the TiO_2 films on the degradation of an azodye in water was studied. The degradation of the initial intense orange color due to the photocatalysis has been followed by near infrared spectroscopy. The results indicated that the TiO_2 thin films modified with TiO_2 nanoparticles and cured with UV and microwave technologies are highly efficient for the removal of the azodye, whereas the films cured only in an oven at low temperatures do not present photocatalytic properties. In conclusion, ultraviolet radiation and microwave heating technologies are clean, cost-effective, energy efficient, faster, and convenient methods of heating, which results in shorter-time reaction times and in TiO2 thin films with improved photocatalytic properties.

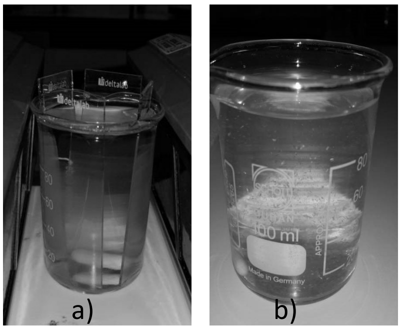

Figure1. Final appearance of the solution treated with a TiO_2 thin film cured: a) in an oven at 150 ºC and b) using microwave.

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Notes

(P3-PS)

OXIDE NANOCRYSTALLITES WITH FACETS OF CONTROLLED ORIENTATION

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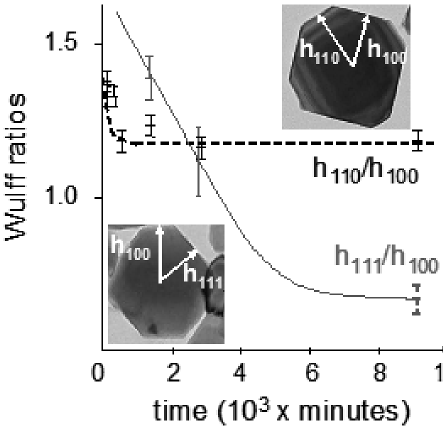
ABSTRACT

In both natural and industrial environments, oxides are currently in the form of nanoparticles which often show complex crystallography. Since properties much rely on structure, oxide nanoparticles with oriented facets are guides for the understanding of orientation-dependent behaviours, possibly by comparison with the surfaces of bulk crystals. Moreover, the combination of analysis in ultra-high vacuum (UHV), in conditions that are usually devoted to study of single crystal surfaces, and in atmospheres close to normal is quite relevant to pinpoint mechanisms at the atomic level with the help of numerical simulations. Examples of MgO, ZnO and TiO_2 nanoparticles are given.

On MgO smoke that mostly involves cubic nanocrystallites closed by (100) facets, low-coordinated sites active in the dissociative adsorption of water are characterized by transmission electron microscopy, photoemission (XPS) and Infrared measurements supported by *ab initio* calculations (Fig. 1). [1-4] Evidence is provided for the modification of the surface structure upon adsorption/desorption of water molecules, which questions the representation of MgO complex surfaces on the basis of a Kossel model.

On ZnO, Infrared spectra collected from UHV to normal pressure allow to decipher specific contributions of the polar (ZnO(0001)-O and ZnO(000-1)-Zn) and non-polar (ZnO(10-10) and ZnO(11-20)) facets during water and hydrogen adsorption. [4]

A challenging issue regarding TiO_2 powders is to characterize by flexible means the various polymorphs, mainly anatase and rutile, that are involved in the material. The existence of spectroscopic fingerprints is discussed by the photoemission analysis of rutile TiO_2(110) and anatase TiO_2(001) surfaces. [5]



$\Gamma/\Gamma_{hydratée(100)}$	Exp.	Théo.
(110)	1,19 ± 0.02	1,14
(111)	0,65 ± 0.05	0,89

Figure 1. Top: MgO cubic smoke crystallites, initially limited by (100) facets. During dissolution in water: emergence of (110) and (111) facets - Bottom: experimental surface energies (relative to (100)) derived from the top profile vs calculated values.

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Notes

(P4-PS)

PREPARATION OF TiO_2 NANOPARTICLES BY PULSED LASER ABLATION IN SURFACTANT SOLUTION

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ABSTRACT

Pulsed laser ablation (irradiation) of targets in liquids (PLAL) is a simple and “green” technique which normally operates in water or organic liquids under ambient conditions. Underlying mechanism of TiO_2 formation by PLAL can be summarized in three–steps: the first step is the generation of plasma due to high–pressure and high–temperature as a result of the interaction of laser with matter. Second step is an ultrasonic adiabatic expansion of the plasma that leads to a quick cooling of the plume region and hence to the formation of titanium clusters. Finally, the plasma is extinguished and formed titanium clusters encounter and interact with the solvent and surfactant molecules in the surrounding solution inducing some chemical reactions [1, 2].

The solvent can provide positive physical and chemical effects such as plasma confinement, cooling actions, oxidation or reduction leading to enhancement of ablation efficiency [1, 3, 4]. *Tilaki et al.* [5] and *Mafune et al.* [6] have prevented nanoparticle for their agglomeration by changing the surfactant and its concentration.

In order to obtain dispersed and stable nanoparticles in solution using the laser ablation method, we employed surfactants for preparation. Ethylenediaminetetraacetic acid (Trilon B); sodium dodecyl sulfate (SDS); polyvinyl alcohol (PVA); glycine (GLY) and other were applied. In Figure 1 are noticed that the most successful application of surfactant in both concentrations (0.001 M, 0.01 M) is attributed to Trilon B.

Almost all produced TiO_2 NPs in DI water and surfactant exhibit large size distribution with diameters ranging 28 to hundreds of nanometers. However, the size distribution is shifted to region of smaller NPs sizes.

All experiments for the synthesis of titania colloidal solutions were carried out with a pulsed Nd:YAG laser beam (Femtosecond Laser system Altse 001, UAB „Altechna”, Lithuania).

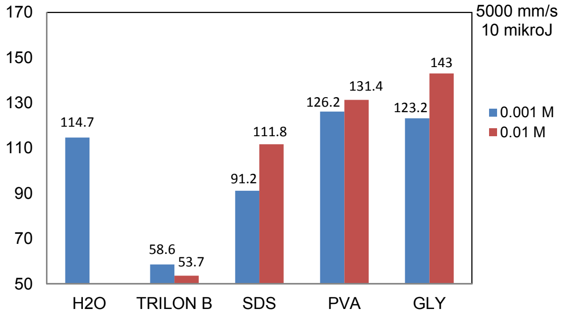

Figure1. Average size of nanoparticles produced by laser ablation of Ti plate in deionized water with the same ablation time (1 hour) laser power 10 μJ and scan rate of 5000 mm/s.

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Notes

(P5-PS)

STUDY OF TiO_2 NANOPARTICLES CRYSTALLINE PHASE BY PULSED LASER ABLATION IN AQUEOUS MEDIA

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ABSTRACT

Since two last decades, pulsed laser ablation (irradiation) of targets in liquids (PLAL) has recently become a promising an efficient physical technique for nanoparticle production due to a number of advantages compared to conventional methods such as simplicity, low production cost and nanoparticle collecting in liquid avoiding the use of vacuum equipment, the absence of chemical reagents in solution, better control over stoichiometry and material variety [1-6]. There are no counter–ions or residuals of reducing agents left in the solution. For this reason laser ablation of solid targets in liquids can be considered as a method of nanoparticle synthesis which is an alternative to chemical methods.

The process proceeds in one step and results in immediate formation of nanoparticles in the liquid in which the target is immersed. We used a solid Ti (99.99 %, Alfa Aesar) plate and characterized the compositions and structures of produced nanoparticles via PLAL in DI water. The X–ray diffraction (XRD) pattern was determined. Figure 1 demonstrates the XRD pattern over a scan interval from 10 to 80^o for the sample of TiO_2 by PLAL. According to the standard diffraction data over the scan interval, it is seen that the XRD data for the sample obtained by PLAL matches the standard rutile, TiO and Ti_2O_3 pattern (JCPDS number: 00–021–1276, 00–012–0754 and 01–071–1047, respectively).

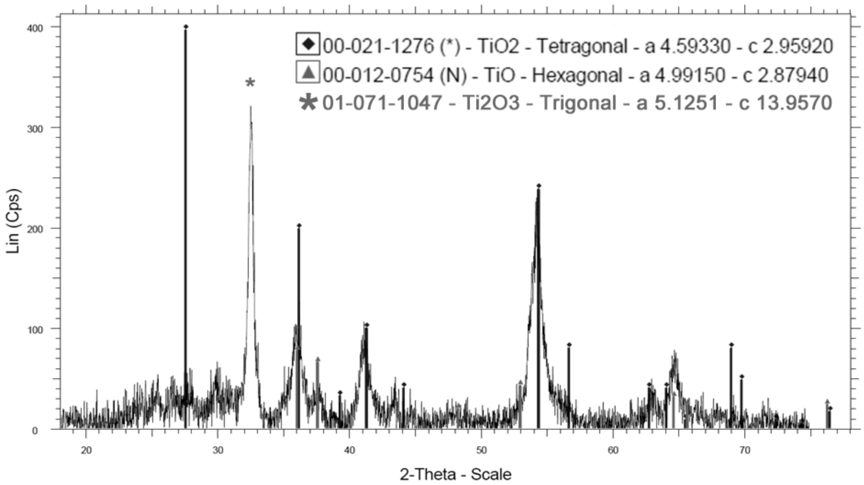

Figure 6. XRD pattern of the TiO_2, TiO and Ti_2O_3 prepared by ablation of Ti plate in DI water.

Anatase, brookite, and rutile are the major crystalline structures of TiO_2, of which rutile phase is most stable; whereas anatase and brookite phases are metastable and easily transformed to rutile phase when heated above about 600–800 ^oC [7]. The formation of rutile phase could be explained as a result of the interaction of laser beam with Ti plate under much higher temperature than 600 ^oC. Depending on the dominant crystalline phase and laser parameters, UV spectra may be different.

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Notes

(P6-PS)

ECOSHOPPING EU PROJECT - PHOTOCATALYTIC ACTIVITY OF COMMERCIAL INDOOR PAINTS VERSUS NEW DOPED TiO_2-BASED COMPOUNDS: INFLUENCE OF EXPERIMENTAL CONDITIONS AND LIGHTING SYSTEMS

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ABSTRACT

EcoShopping project (Energy efficient & Cost competitive retrofitting solutions for Shopping buildings) aims to build a holistic retrofitting solution for commercial buildings to reduce primary energy consumption down to less than 80kWh/m^2 per year and increase the share of RES (Renewable Energy Sources) more than 50% compared to the state of the art [1]. The approach is systemic by developing the most suitable solution for different applications. As some examples: novel thermal insulation solutions; easy to install and cascadable daylighting technologies; heating, ventilation and air conditioning retrofitting systemic approach based on RES; integrated solution way based on the intelligent automation unit concept.

Indoor air quality, moreover, represents one of the most crucial aspects for a high level wellness and it needs to be strictly controlled. Photocatalytic - self-cleaning paints represent a considerable smart and economical solution for indoor pollutants removal. The self-cleaning action, indeed, involves the mineralization of organic compounds, thus obtaining carbon dioxide and water as final products. The oxidation process of self-cleanings paints, of course, is also applicable to biological contamination, such as moulds, by degradation of cellular membrane [2-4].

Three photocatalytic indoor commercial paints were selected taking into account the technical sheets provided by the producers, with special consideration with respect to the required lighting system for the photocatalytic action execution. Commercial paints were fully characterized in order to obtain a composition-photoactivity correlation. The new developed TiO_2-based photocatalysts were prepared for obtaining an improved photoactivity and a more extended exploitation of the visible light.

The commercial paints were then compared to new-developed TiO_2 based photocatalysts and tested under different experimental conditions (pH and organic pollutant probes) and different lighting systems (UVA, UVC, Xenon, fluorescent and LED lamps) in order to evaluate the actual photocatalytic properties. Degussa P25 was always employed as standard reference for comparison. The results show that the new compounds offer an improved activity with respect to P25 and with respect to the commercial paints in acidic condition. It was also proved that the photocatalytic activity depends on the target molecule and, as a consequence, on the experimental conditions.

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Notes

(P7-PS)

A CHEMOMETRIC APPROACH FOR CLASSIFICATION AND QUANTIFICATION OF DIFFERENT CRYSTALLINE PHASES OF TiO_2 NANOPARTICLES MIXTURES THROUGH RAMAN SPECTROSCOPY

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ABSTRACT

In this work, we report the development of a chemometrics tools for classification and quantification of different TiO_2 crystalline phases in binary mixtures analized by Raman spectroscopy. TiO_2 occurs as three different polymorphs: anatase, rutile, and brookite. Due to the different spatial organization, these polymorphs exhibit different physical chemical properties, such stability, photocatalytic activity, refractive index, etc. The mixing of different phases, in particular anatase and rutile, has been reported to exhibit enhanced photoactivity, in comparison with pure phase [1]. For this reason, abetter knowledge of mixtures composition becomes essential in many fields (i.e. photocatalysis, production, etc.).

The develop a solid method able to quantify different phases amount in TiO_2 NPs mixtures represent one of the main goals of the European FP7 project SETNanoMetro.

Raman spectroscopy analysis represents a rapid and simple method to distinguish different crystallographic structures of the same compound. For the powders homogenization, wet mixing and sonication was chosen[2]. Suspensions were dried and then analyzed by raman spectroscopy using mapping mode. Raman mapping is conducted in order to overcome the potential inhomogeneity of the discrete mixture of powders at nano and micrometric scale.

The mean Raman spectra of sample maps are subjected to chemometric analysis using TQ AnalystTM 8.0 software (ThermoFisher Scientific, Waltham, USA). A multivariate approach is chosen in order to compensate surface irregularity.

Raman spectra of pure phases and spectra of well-known mixtures are collected and then used as calibration standards for a chemometric treatment of data.

Discriminant Analysis method is employed to separate mixtures (anatase/brookite, anatase/rutile, and rutile/brookite) from pure samples. The chemometric approach used for the classification is a supervised cluster analysis whose task is grouping a set of objects in such a way that objects in the same cluster are more similar to each other than to those of other clusters [3].

The Partial Least Squares (PLS) method is used for the quantitative calibration and three predictive methods are obtained for the mixtures fractions quantification [4].

In order to validate the methods, the goodness of the models was tested using external validation samples.

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Notes

(P8-PS)

FABRICATION OF HIGHLY REPRODUCIBLE AND LONG LIFETIME TIPS FOR TIP-ENHANCED RAMAN SPECTROSCOPY BY ELECTRON BEAM PHYSICAL VAPOR DEPOSITION

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ABSTRACT

Tip-enhanced Raman spectroscopy[1] (TERS) is a pioneering imaging technique that combines surface-enhanced Raman spectroscopy with scanning probe microscopy (SPM) resolution. At present, it is the only one technique able to provide simultaneously both chemical and morphological imaging of a sample at the nanoscale.

In order to enhance the Raman signal of a sample, TERS uses localized surface plasmons generated by a laser on the apex of a sharp metal-coated SPM tip. TERS-active tips for atomic force microscopy (AFM) mode TERS are usually made by evaporation of noble metals, like Au or Ag, on commercial AFM cantilevers. Unfortunately, the tips usually undergo rapid both chemical and mechanical degradation, which strongly limits the widespread use of TERS as a competitive market technology.

In this work, a fabrication method of TERS tips based on electron gun physical vapor deposition (EGPVD) is presented. The method was tested on both conventional AFM tips for transmission-mode TERS and on top visual probes for upright configurations. In both cases, EGPVD produces highly reproducible metallization and dielectric coatings, leading to TERS-active tips which were proved to survive even 5 months after fabrication.

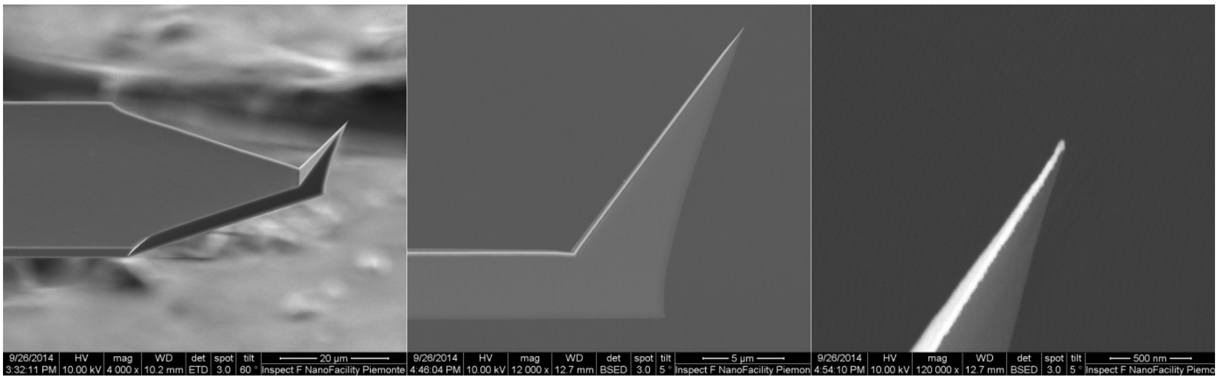

Figure1. Tilted and cross sectional scanning electron microscopy images of Au-coated top visual AFM tips fabricated by EGPVD for TERS.

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Notes

(P9-PS)

STRUCTURAL CHARACTERIZATION OF SHAPE-ENGINEERED TiO_2 NANOPARTICLES BY XRD AND SAED

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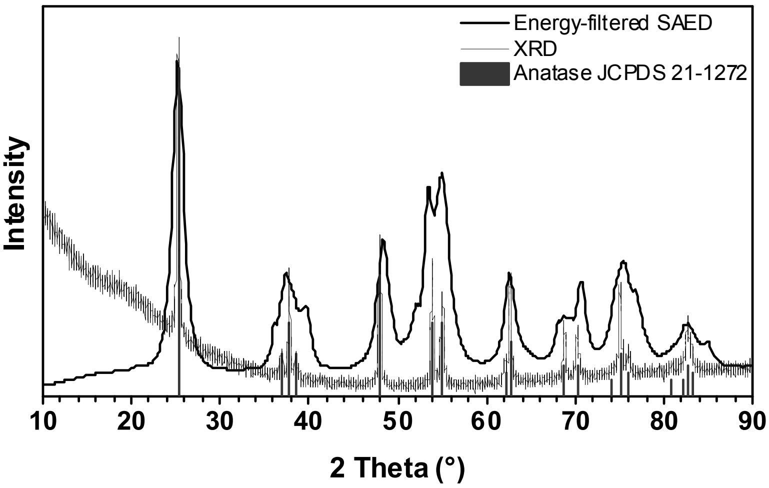
ABSTRACT

The phase identification of crystalline powder and bulk materials is easy to determine by means of X-ray diffraction (XRD) or selected area electron diffraction (SAED) in a transmission electron microscope (TEM).[1] However, a routine structural characterization of nanoparticles (NP) with a nano-crystal size below 100 nm is still challenging. In particular, a standardless quantitative phase analysis to determine the crystalline/amorphous fraction of a nanocrystalline material is subject to ongoing research.[2]

We present a characterization routine for the determination of the phase composition of TiO_2 NPs as powder and films by using XRD and SAED. Moreover, we discuss a proposal for the estimation of the crystalline/amorphous fraction of TiO_2 NPs based on SAED patterns. The independently determined phase fractions from XRD and SEAD analysis are compared and discussed.

In this study shape-engineered TiO_2 NPs with truncated bipyramidal morphology of 55 nm x 30 nm (length and width) was used. The XRD experiments were carried out in transmission geometry. The SAED patterns were collected using an energy-filtered TEM. To identify the crystalline phases both the measured X-ray and the electron diffraction patterns of the samples were compared to the JCPDS database. To quantify the phase fraction, the XRD and SAED patterns were deconvoluted with specific fitting procedures which take into account an amorphous and crystalline phase.

Figure 1 presents an overlap of TiO_2 NP patterns obtained from XRD and SAED compared with JCPDS data of peak positions for TiO_2 anatase (21-1272). The peak positions of the XRD and SEAD patterns show a high conformity to the TiO_2 anatase phase. The standardless quantitative phase analysis results in a crystalline/amorphous fraction of 89%/11%. The analysis routine and the measurement uncertainties associated to both XRD and SAED results will be discussed.



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Notes

(P10-PS)

HT SYNTHETIC PROCEDURES FOR SHAPE AND SIZE CONTROLLED ANATASE NP$_s$

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ABSTRACT

The synthesis of TiO_2 nanoparticles (NPs) with well-defined morphology and size is fundamental for the development of advanced nanomaterials in various application fields: photocatalysis, photovoltaics, sensors, bone-implants with enhanced bone integration [1,2]…

Synthetic routes were developed for bipyramidal TiO_2 facet-controlled anatase NPs with low truncation along the c-axis and acicular morphology, through hydrothermal treatments (HT) of aqueous solutions of Ti(IV)(triethanolamine)$_2$ (Ti(TEOA)$_2$) [3,4].

The Ti(TEOA)$_2$ was prepared by dropping Ti(IV) isopropoxide into triethanolamine. The isopropyl alcohol was then distilled off. A preliminary characterization of a methanolic solution of this compound was carried out by Electrospray Ionization – High Resolution Mass Spectrometry (ESI-HRMS).

The formation of anatase (101) surfaces is favoured by the presence of OH ligands, including water. Therefore the shape control agents used were pH and triethanolamine.

Bipyramidal TiO_2 anatase NPs with low truncation along the c-axis (mainly (101) facets exposed) and with dimensional polydispersity in the 5-20% range were produced, along with the procedure and the process parameters (pH, temperature and reagent concentrations) to modulate the NP size along the c-axis in the 20-60 nm range.

Acicular TiO_2 anatase NPs (with shape factor c/a = 5.5 and a certain amount of (100) facets exposed) were also obtained from hydrothermal treatments at high pH and low temperature.

The dimensional characterization of the synthesized NPs was carried out by dynamic light scattering measurements (DLS); the comparison between the DLS data and the size data obtained from the characterization via transmission scanning electron microscopy (T-SEM) allowed a valid interpretation of all the DLS data obtained and established an accurate procedure for the data evaluation.

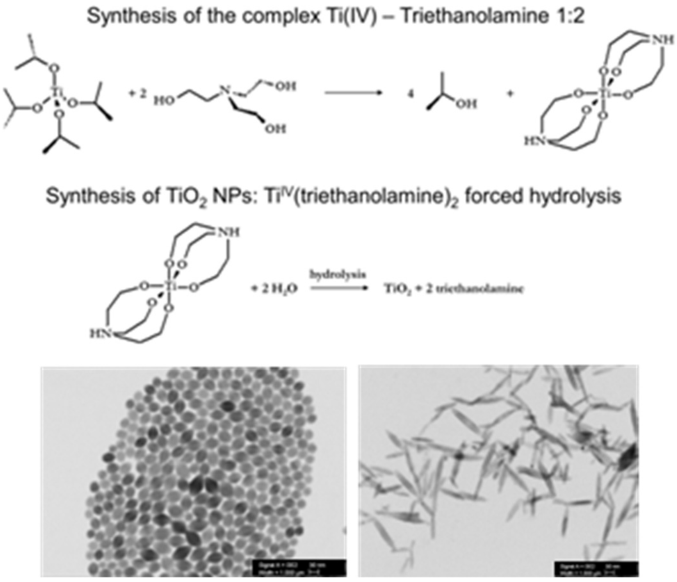

Figure1. Scheme of the Ti(TEOA)$_2$ and the TiO_2 anatase NP syntheses (top); T-SEM micrographs of truncated bipyramidal TiO_2 NPs (bottom left) and acicular TiO_2 NPs (bottom right).

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Notes

(P11-PS)

EQUILIBRIUM SHAPE OF SUPPORTED SILVER CLUSTERS

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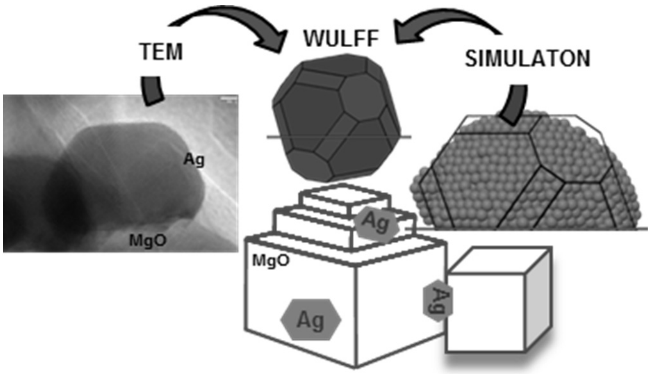
ABSTRACT

Metallic nanoparticles embedded in an oxide substrate or supported on its surface are encountered in a large number of applications. Best known examples are catalysis, environmental chemistry, plasmonics, magnetic information storage and medical applications. Broad spectrum of applications results from properties that are strongly determined by their size, shape and crystallographic orientation of exposed facets.

We studded the morphology of silver nanoparticles supported on MgO smoke crystallites by combining Transmission Electron Microscopy (TEM) and atomistic simulations of clusters of realistic size [1]. An advantage was taken of the occurrence of complex – but well-defined – MgO surfaces to analyze Ag clusters of various orientations. Silver clusters were seen to adopt systematically the shape of a truncated octahedron irrespectively of the supports' morphology (Fig.1). The (100)Ag//(100)MgO epitaxy was evidenced and (100), (111) and (110) facets were identified. The agreement between observed shapes and simulated profiles demonstrated that the formers were close to equilibrium which allowed the use of Wulff-Kaishew construction (Fig.1) to determine the anisotropy ratios ⍰100/⍰111 (1.03±0.03) and ⍰110/⍰111 (1.08±0.03) and Ag(100)/MgO(100) adhesion energy (0.58±0.10 J.m-2) for clusters large enough to escape stress effects.

The existence of the open (110) facet in the case of silver raise the question of its occurrence in the equilibrium shape of clusters of other fcc metals. Moreover, the existing experimental and theoretical evidence is somewhat contradictory in case of Au clusters. Preliminary results will be presented in this regard.



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Notes

Session 4 (S4)

Nanoparticles, films & light: energy and imaging

(KN-S4)

PREPARATION OF METAL OXIDES ELECTRODES AND ORGANIC SENSITIZERS FOR THE FABRICATION OF EFFICIENT DYE-SENSITIZED SOLAR CELLS

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ABSTRACT

Tremendous progress that has been achieved in the past decade regarding the efficiency of Dye-Sensitized Solar Cells (DSSC) is associated with the development of new materials to fabricate them. With record efficiency over 12%, [1] DSSCs appear now as a realistic approach for building-integrated photovoltaics (BIPV). In order to improve their performances and to increase their commercial attractiveness, several strategies have been recently developed. The first one consists in developing new nanomaterials based on metal oxides with potentially higher electron mobility to replace TiO_2 which is routinely used for their fabrication. The second strategy consists in developing cheap, colorful, stable and highly efficient organic dyes to replace ruthenium-based complexes classically employed for the sensitization of the electrodes.

In this work we will present several approaches for the preparation of Zinc-based binary and ternary metal oxides nanoparticles (nanowires, nanofibers) and their use for the fabrication of DSSC. We will present also the synthesis of purely organic dyes, alternatives to ruthenium-based sensitizers, specifically designed for the sensitization of these electrodes and we will show that rather good performances can be achieved using this strategy.[2-3]

In the second part of this lecture we will demonstrate that when these dyes are combined with TiO_2 mesoporous electrodes, highly efficient solar cells can be achieved with current densities up to 20 mA/cm² and power conversion efficiency up to 10.2 %, under standard conditions. After optimization of the device fabrication, solar cells demonstrate a high stability over more than 9000 h upon light soaking at 1 sun, 1000 W/m² and upon heating at 65 °C. Some results obtained when the dyes are incorporated in solar modules will also be presented.[4]

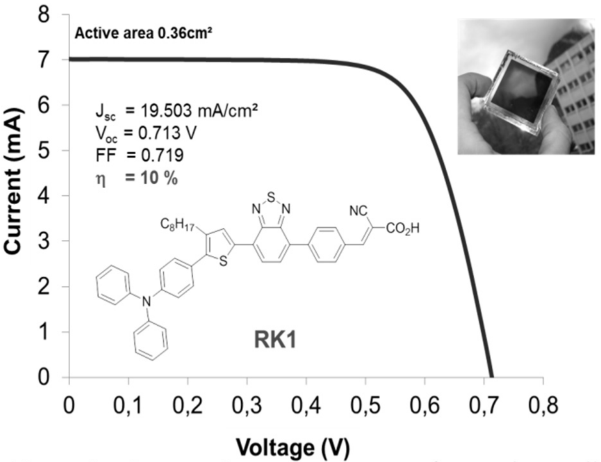

Figure1. Current-Voltage curve of a solar cell containing a macro-channel TiO2 mesoporous electrode sensitized by an organic dye

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Notes

(O1-S4)

BARE AND SILICA-COVERED GOLD NANOPARTICLES: A SUITABLE TOOL FOR PESTICIDE DETECTION THROUGH RAMAN SPECTROSCOPY

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ABSTRACT

Gold nanoparticles (AuNPs) play a determinant role in several sensors applications. In particular their plasmon activity can be exploited to enhance Raman signals of molecules localized close to their surfaces, phenomenon known as Surface-Enhanced Raman Scattering (SERS) effect. SERS technique is a powerful tool for traces analysis, which combines the fingerprint characterization of analytes with high sensitivity, thanks to the enhancement caused by nanostructured noble metals. Fast detection of surface contaminants is carried out by spreading AuNPs on samples and collecting Raman spectra.

The control over nanoparticles main features, such as size, shape, surface area and size distribution, ensures greater reliability and accuracy of SERS analysis. On the other hand gold nanoparticles manage to interact with the substances on sample surface. This chemical interaction modifies the spectra of contaminants, making them difficult to interpret. In order to overcome this problem, AuNPs are covered by a silica shell through an easy functionalization process [1]. The thin coating keeps the nanoparticles from agglomerating, separates them from direct contact with the probed material and allows the nanoparticles to conform to different contours of substrates [2].

Bare and silica-covered nanoparticles, well known as SHINs (Shell-Isolated Nanoparticles), are employed in a SERS system that manages to detect fungicide in very low concentration on different surfaces. For this study pyrimethanil was chosen as representative test material. Pyrimethanil is an active ingredient of a commonly used pesticide, which is employed on several horticultural species. It was included in Annex I to Directive 91/414/EEC on 01 June 2007 and recently EFSA (European Food Safety Authority) has been required to provide a reasoned opinion on the review of the existing MRLs (Maximum Residue Levels) for this active substance [3]. Uniform films of diluted pesticide are realized by spin coating method on Si/SiO_2 wafers. Then the coated substrates are used to attest the SERS effect with pyrimethanil. Bare and SHINs nanoparticles are dropped on the substrate surface and dried under vacuum. Only Raman spectra collected into the gold nanoparticles drop show the characteristic pyrimethanil signals, at 1300 cm^{-1}, 1240 cm^{-1} and 620 cm^{-1}. The main goal of the work is to put a SERS system to use for detection of pesticide traces on fruits peels. This rapid analytic procedure may answer to the consumers requests of horticultural products safety.

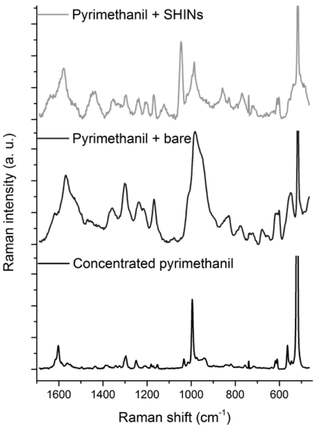

Figure 1 Raman spectrum of concentrated pyrimethanil (black spectrum), SERS spectra of diluted pyrimethanil collected close to AuNps (blue spectrum) and to SHINs (green spectrum)

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Notes

(O2-S4)

HYBRID FLUORESCENT DYE-SILICA NANOPARTICLES: TOWARD A POSSIBLE MOLECULAR ENGINEERING

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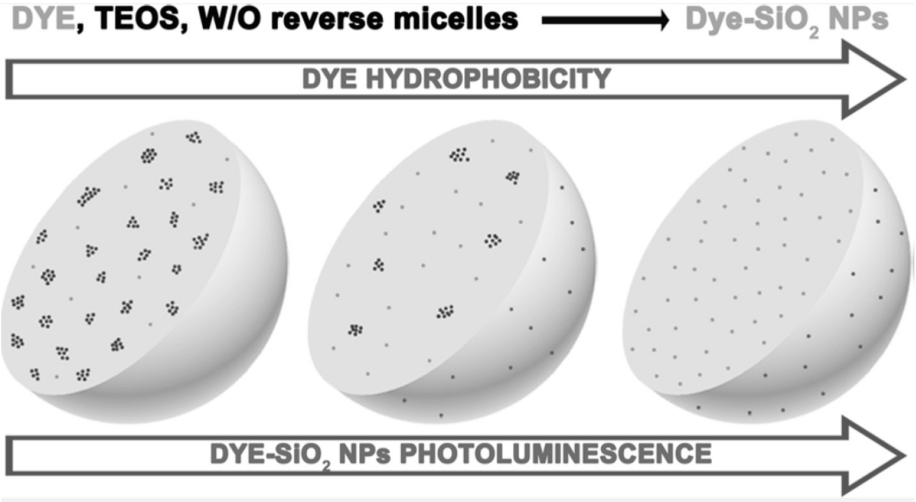
ABSTRACT

This work was addressed to the elucidation of molecular parameters that rule the distribution of organic fluorophores throughout the nascent inorganic network during the synthesis of hybrid dye-silica nanoparticles by the reverse microemulsion method, that involves the partition of reactants among bulk oil phase, surfactant palisade and inner water core. The evolution of the photophysical properties (absorption, steady state and time-resolved photoluminescence) of three cyanine dyes, differing for the number of sulfonic substituents, from the starting microemulsion to the final nanoparticles provided evidence of the key role of the hydrophilicity of the fluorophores in ruling the dispersion within the nascent SiO_2 matrix [1].



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Notes

(O3-S4)

INDUSTRIAL DEVELOPMENT OF DYE SENSITIZED SOLAR CELLS

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ABSTRACT

Dye-sensitised solar cells are a disruptive photovoltaic technology using nano-composites of mesoporous TiO_2 and dyes (typically Ruthenium complexes); they created a break- through by achieving relatively high conversion efficiency through the use of inexpensive and abundant materials [1]. In these devices, solar cell action is initiated upon the illumination of light by excitonic electron-hole pair generation and dissociation leading to a charge separation at the nano-interface. These devices are therefore termed as 'Excitonic' or 'Organic–Inorganic' or 'Hybrid' Solar Cells. Unlike conventional p–n homojunction (c-Si) solar cells, the absorption of photons on one hand, and the electronic transport, on the other hand, are mediated via two dissimilar constituents viz. dyes and n-type nanocrystalline TiO_2, respectively.

Dye-sensitised solar cell (DSSC) technology has seen some radical advancement recently owing to the new materials and device structure innovations. The efficiency increase in the solid state version of DSSCs from about 5% to over 19% [2] have been reported within two years of time scale, which comes mainly from the efforts in the perovskites based mesoporous solar cells developments. This has increased its potential significantly to become a low cost alternative for commercially available solar cell technologies. The progress of the liquid junction based DSSCs towards their better performance and stability had been relatively slower and was coupled with scale up and engineering challenges such as encapsulation, sealing of the device, etc.

The recent developments on the solid state DSSCs have given a solid belief for this technology to make a mark towards its commercialisation. Although a great progress in the device efficiency has been made, a lot of efforts are still needed to break the barriers that had been preventing this from penetrating the market. An attempt will be made through this communication to report the recent advances in the liquid junction, and the industrial developments that led to the fabrication of the first multicolour DSSC façade.

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Notes

Special Session (SS)

Standardization
and Equipment

(O1-SS)

STANDARDIZATION IN THE AREA OF NANOTECHNOLOGY

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ABSTRACT

Like in the whole material science there is a need for standardization in the area of nanotechnology because of the need to be able to compare measurement results. This is especially true in respect to the public discussion concerning human and ecotoxicological risks of the products. In an ideal case the physical and chemical characteristics of the test objects are determined with standardized test methods including standardized reporting sheets and the same should be true for toxicological test methods. Only comparable test results can be considered valuable in this context. In research projects financed by the European Commission there is also a growing pressure to use standardization as exploitation possibility to ensure that the project results are usable and kept available to a broader audience.

A lot of standardization committees in the International Standardization Organization ISO and the European Standardization Committee CEN are dealing with nanotechnology but some of them are of particular interest. These committees are ISO/TC 229 "Nanotechnologies", ISO/TC 24/SC 4 "Particle Size Measurement" and CEN/TC 352 "Nanotechnologies". While ISO/TC 24/SC 4 is more focused on instrumentation the scopes of ISOTC 229 and CEN/TC 352 are broader. Both committees are dedicated to the development of standardized measurement procedures for physical and chemical characterization of nano-objects and nanostructured materials as well as of measurement procedures for the determination of the toxicological effects of nanomaterials to humans and ecology including risk assessment and life cycle assessment.

In order to ensure the repeatability and reproducibility of test methods the quality of the procedures in the nanotechnology sector must be well reported. ISO/TC 229 requests for each test method proposed as new work item a metrological check-list to be filled in. So, e. g. information about interlaboratory tests and uncertainty budgets are requested. SETNanoMetro will perform own interlaboratory test and additionally join interlaboratory comparisons at VAMAS.

The usual way to participate in european or international standardization is the delegation through National Standardization Bodies. At CEN, it is possible for a research project to apply for a "Project Liaison". SETNanoMetro applied for a Project Liaison with CEN/TC 352 and is therefore allowed to attend all plenary meetings and to propose new work items during its lifetime. The direct participation of research projects at ISO is impossible. SETNanoMetro will join relevant national standardization committees which mirror the respective ISO committee to apply for new work items or to work on ongoing standardization projects of interest.

Another obstacle for a research project is to find the correct Technical Committee (TC) the project result would fit to. At SETNanoMetro the German national standardization body DIN is participating as a partner in the Consortium and helped to identify CEN/TC 352, CEN/TC 386, ISO/TC 229, ISO/TC 24/SC 4 as possible standardization partners from the start. A continuous monitoring is refining the selection during the lifetime of the project. If there is no National Standardization Body involved in the project it is possible to contact the nanoSTAIR platform [1] which offers support. In addition each Institution can contact its National Standardization Body and ask for support.

New work item proposals for new standards and the standards themselves are written in special forms and templates following specific and strict rules and following a specific process. DIN is navigating SETNanoMetro through this procedure. Research projects without a national standardization body as partner or standardization experience can ask nanoSTAIR or National Standardization Bodies for support.

REFERENCES

[1] http://www.nanostair.eu-vri.eu/

Notes

(O2-SS)

INNOVATIVE SOLUTIONS FOR DEMANDING FT-IR APPLICATIONS

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ABSTRACT

Some examples will be shown in order to demonstrate the state of the art of the FT-IR Spectroscopy when applied to solids and gases. In particular will be shown the possibility to analyze a sample under vacuum condition covering a broad spectral range from Mid IR to Far IR using innovative optical components. The possibility to follow fast gas absorptions will be discussed showing the temporal resolution achievable up today. All the software innovative issues regarding temporal acquisition will be shown. Finally, all the sampling possibilities related to the smallest FT-IR spectrometer, usable also into a glove box, in our product line will be discussed.

Notes

(O3-SS)

A NEW APPROACH TO RAMAN IMAGING → MOVING FROM SPECTRA TO IMAGE

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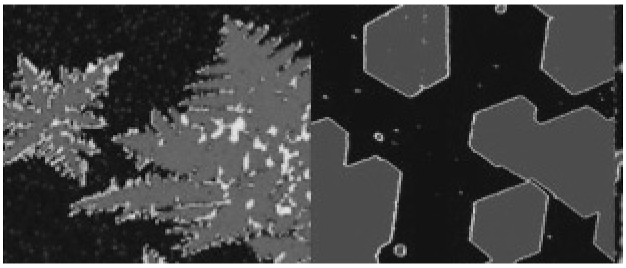
ABSTRACT

Raman imaging is an essential tool for material scientists and nano-materials researchers, providing rich chemical information and structural detail for a broad range of applications. New advances in Raman instrumentation are allowing for faster, more sensitive Raman imaging measurements. This presentation will introduce a unique image centric approach to Raman imaging employed by the new Thermo Scientific™ DXR™xi Raman imaging microscope. You will see how new realtime interpretation and analysis tools coupled with this image centric approach fosters a more intelligent and efficient route for setting up your experiment, shortening your journey from questions to answer.



Notes

(O4-SS)

A SINGLE-WALLED CARBON NANOTUBE REFERENCE SAMPLE FOR OPTICAL CONTRAST AND SPATIAL RESOLUTION IN TIP-ENHANCED RAMAN SPECTROSCOPY

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ABSTRACT

Tip-enhanced Raman spectroscopy (TERS) is a pioneering nanoimaging technique that combines surface-enhanced Raman spectroscopy with Raman-AFM analysis. The aim of the present study is to use a single-walled carbon nanotube (SWCNT) to measure the spatial resolution in TERS, the degree of accuracy up to metrological levels to propose the sample as a new standard reference material for this cutting-edge technology.

A one-dimensional nanostructure such as a SWCNT is an ideal candidate to give reference for the spatial resolution in TERS. Indeed, SWCNTs are very good Raman scatterers and have diameters close to about 1 nm, which is at least 10 times less the diameter of a sharp TERS tip. In particular, the SWCNTs used in the present work are certified reference materials from the National Institute of Standard and Technology (NIST), deposited by the Istituto Nazionale di Ricerca Metrologica (INRIM) onto glass cover slips for transmission-mode TERS, the measurements carried out at the National Physical Laboratory (NPL).

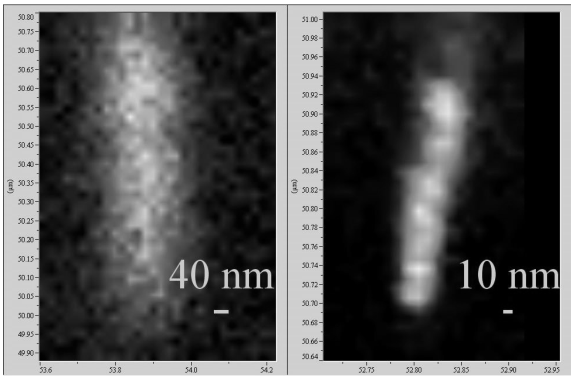

Figure1. Confocal (blue) and TERS (orange) images of a SWCNT.

According to literature [1], SWCNTs can be worthwhile systems allowing the estimation of consistent values for the optical contrast, thus the enhancement factor (EF) in TERS. In [1], the huge variability in the values of the EF reported in literature until then was pointed out, even for the same combination of tip material and excitation laser wavelength used in a TERS experiment. For instance, only considering SWCNTs as samples, the EF values varied between 30 and 105 (Table 1 in [1]), suggesting a clear need for a systematic evaluation of the EFs. The main cause of these massive discrepancies was found to be due to overestimations of EFs because of different far-field Raman signal contributions. Therefore, a simple methodology able to extract, directly from a TERS map, a consistent value of EF was proposed to overcome reproducibility and repeatability issues between different laboratories. The methodology was based on separating the near-field from the far-field contributions in the cross sectional profile of the Raman image of SWCNTs, where they result combined. Since the optical spatial resolution in TERS can be determined from such profile of the near-field Raman image, as the width of the signal full width at half maximum, the isolation of the real near-field contribution from a SWCNT alone is essential for metrological purposes. Also, this method does not require another measurement to subtract the far-field background, as this information is contained in the near-field one already, and it is thus extracted. The proof of concept of this study, however, was only demonstrated by comparing the EFs calculated from two TERS images of bundles of SWCNTs, from two different laboratories. The technological progress achieved both in TERS measurements and samples fabrication allows to repeat the same calculation today, but on an isolated SWCNT.

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Notes

Session 5 (S5)

Nanoparticles, films & light: photocatalysis

(KN-S5)

PHOTOCATALYSIS: GOING FROM THE LAB TO THE ROOF

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ABSTRACT

TiO_2 has been known for its photocatalytic properties for decades. First described by Akira Fujishima in the late 60's. The commercial potential was from the beginning recognized as being substantial and a lot of effort was invested in the area, especially in Japan, but the rest of the world followed quite fast.

In the academic world the photocatalytic effect is very well know and fully accepted as a solid research area. From a commercial point of view the photocatalytic phenomenon is still quite new (except from maybe in Japan) and even though several products exist the public is still not fully aware of the potential of this.

Besides the water splitting effect, the two main areas, from a commercial point of view, is self-cleaning and VOC/NOx removal.

The self-cleaning effect can result in products like windows you do not need to clean; facade materials and road signs that stay sharp; non fogging mirrors and roofing materials with very low alga grow.

The photocatalytic degradation of VOC/NOx is properly the most important part of TiO_2 (still from a commercial point of view) and may be one of the corner stones in pollution handling in the cities.

Thus, it is possible to remove a substantial part of the pollution in urban areas by using construction materials with a photocatalytic effect. It could be roofing materials, facade materials, pavements stones, asphalt areas etc.

Photocat A/S is a company specialized in bringing the photocatalytic effect into various materials, however with a main focus on construction materials. We produce the materials in-house, and often help the customers in the integration process. This talk will partly be about how we produce and modify TiO_2 to fulfill our needs, but mainly on case studies describing all the problems one have when moving from the lab to the factory.

Different products with photocatalytic properties. Pavement stones, roofing material, flooring, windows, foils and bitumen.

Notes

(O1-S5)

PHOTOCATALYTIC PROPERTIES OF TiO_2 NANO PARTICLES

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ABSTRACT

The photocatalytic behaviour of TiO_2, especially in anatase form, is heavily investigated due to various possible applications including solar cell, air- and water purification, biomedical application to mention few. Light, photon, with energy equal and higher than the band gap of the TiO_2 can initiated photocatalytic process. The photon excites an electron from the valence band to the conduction band created electron/hole pair with high redox and oxidation powder. The electron and hole can be collected as electricity or being used for self-cleaning process

The photocatalytic TiO_2 are as coatings or in powder form depending on the applications. The high surfaces area of Nano-scale powder is very attractive for increasing the photocatalytic efficiency. The studies on TiO_2 powders have focused on improving the photocatalytic activity and reducing its band gap. The photocatalytic properties of TiO2 is tailored with optimisation of: preferential oriented crystal structure with higher ratio of 001 compared to 101, coupling with other nano particles, and doping.

This paper describes the investigation on the photocatalytic activity of TiO2 Nano-powders prepared by various routes. The band gap of the powder was measured at individual particle spot using Electron Energy Loss Spectroscopy (EELS) method and correlated with the band gap measured on bulk powder using diffuse reflectance. Transmission electron microscopy (TEM) was used identify the crystal structure and correlated with macroscopic techniques such as XRD and Raman. The photocatalytic activity of the power was characterised using organic dye decomposition method and electrochemistry. Results showed a good correlation between the results from nano and macro methods and provided a holistic indication of the photocatalytic activity of powders and processing routes.

Notes

(O2-S5)

INFLUENCE OF AGGREGATION ON THE PHOTOCATALYTIC ACTIVITY OF TiO_2 NANOPARTICLES

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ABSTRACT

Particle aggregation and agglomeration influence the optical properties of materials and therefore their ability to absorb and scatter the incoming radiation. It is long known that the TiO_2 particle size can influence the photocatalytic activity [1,2]. We have studied the correlation between aggregation and photocatalytic activity for titanium dioxide by means of experimental measurements of extinction and photocatalytic activity and calculations of their optical properties (extinction, absorption and scattering cross-sections). This approach can be adopted to quantitatively assess the quantum yields of the heterogeneous photocatalytic systems.

The study was performed on TiO_2 PC105 Cristal ACTiV™, constituted by aggregated (and agglomerated) primary particles of anatase. The size of the aggregates has been reduced by ultra-sonication. Aqueous suspensions of the obtained materials were characterized by measuring the optical properties (UV-Vis extinction), the sizing properties (DLS) and the photocatalytic activity (degradation kinetics of phenol under standard conditions). The extinction and absorption coefficients of nanoparticles and aggregates were calculated using a code [3] based on the "T-matrix"[4,5], by making use of the Mie theory. The extinction and absorption spectra of the suspensions were derived from the calculated coefficients, considering also the size distributions measured by DLS. Light absorption is maximized when particle aggregation and agglomeration is avoided, while diffusion of the incoming radiation dominates when large aggregates are present in aqueous suspension of TiO_2. The present paper represents a valuable approach to the accurate and reproducible measurement of the photocatalytic activity of TiO_2 nanoparticles suspensions, thus allowing a more reliable comparison of the properties of different materials.

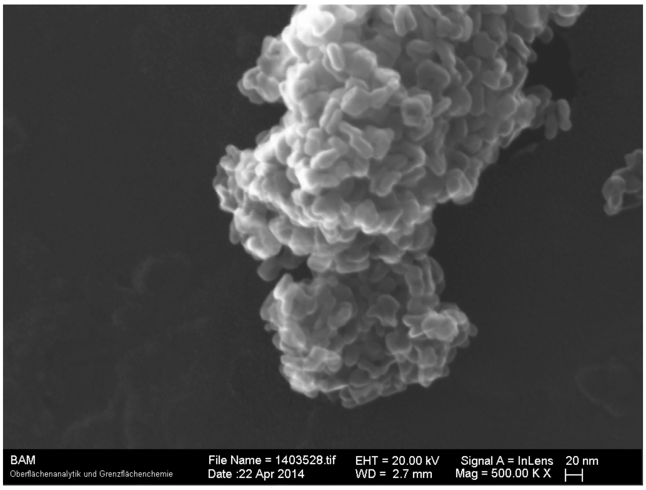

Figure 1 SEM micrograph of PC105 Cristal ACTiV™ as an TiO_2 NPs agglomerate/aggregate.

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Notes

(O3-S5)

ESTABLISHING TRACEABILITY IN KELVIN PROBE MEASUREMENTS FOR PHOTOCATALITIC SURFACES

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ABSTRACT

Kelvin probe force microscopy (KPFM) is a variant of atomic force microscopy (AFM) widely used for examining electrical properties of a surface such as the photocatalytic activity [1]. Unfortunately, KPFM does not provide direct information about the work function of the surface under study, but the so-called contact potential difference (V_{cpd}) between the scanned surface and the AFM tip. In other words, the measured potentials are relative to the surface potential of the tip, which is in principle unknown. In order to establish traceability and obtain absolute results out of a KPFM measurement, comparable to other experiments, it is necessary to determine the surface potential of the tip. A reference sample consisting of an epitaxial multilayer of electroplated metals Ni and Au on a Cu substrate has been used for this purpose together with a calibration procedure that makes it also possible to realize the surface potentials of the scanned materials. The calibration procedure relies on electrochemical measurements of the reference sample (see Ref. [2] for a similar approach). Possible measurement artefacts such as the tip degradation resulting from continuous usage are discussed, and typical biases introduced by different KPFM techniques [3], e.g. due to the differences in lateral and vertical resolution, are pinpointed. The study is supplemented with an uncertainty budget that estimates the overall reproducibility of the measured results and a set of 3D images demonstrating the changes of surface potential of TiO2 particles when exposed to UV light.

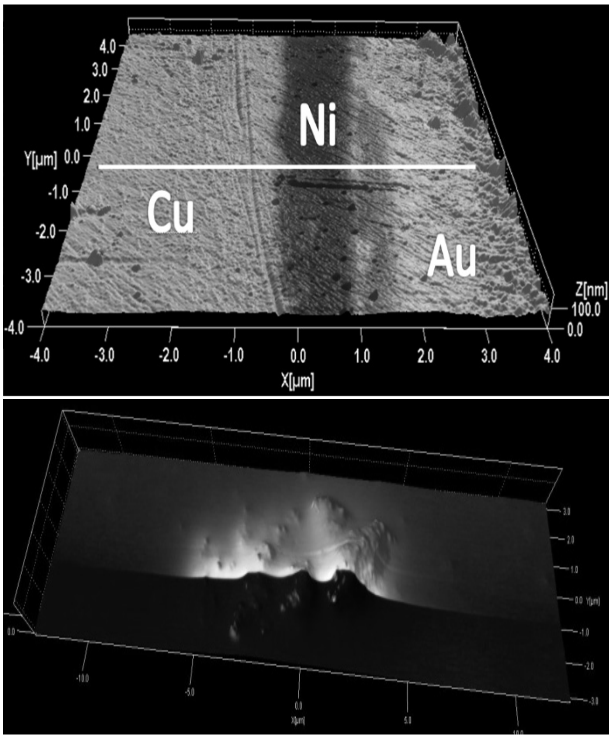

Figure1. AFM images of sample topography with superimposed colouring representing the different surface potentials: reference sample (top), cluster of TiO_2 particles partly exposed to UV light (bottom).

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Notes

(O4-S5)

INVESTIGATION ON PHOTOCATLYTIC TiO_2 COATINGS PRODUCED BY MAGNETRON SPUTTERING PROCESS

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ABSTRACT

In recent years, there has been considerable interest in the use of self-cleaning surfaces on structural materials for various engineering applications. The industrial sectors such as architecture, health and food have considerable interest in exploring the benefits of self-cleaning function to increase visual appearance, air purification, and to obtain hygiene surfaces.

This paper presents an overview of the investigation carried out on magnetron sputtered TiO_2 coatings on aluminium alloy and steel substrate as a function of various parameters including substrate surface finish, coating thickness, and sputtering parameters. Effect of these parameters on the photocatalytic activity was investigated using methods such as high-resolution electron microscopy such as FEG-SEM, FIB, and TEM, AFM, SKPFM, DC polarization methods and AC impedance measurements. Photocatalytic effect was also investigated under wet condition using methylene blue decomposition, while in gas phase using a combination of Quartz Crystal Microbalance (QCM) with TiO_2 coated crystals and measurement of carbon dioxide due to the decomposition of the organic compounds.

In general results show that the photocatalytic activity increases exponentially with increase in thickness of the coating, while saturation is attained above a thickness level, for a given wavelength and intensity of light, due to the diffusion length and the lifetime of the electron and holes formed in the TiO_2 coating. Impedance measurement shows linear increase in capacitance with thickness of TiO_2. Photocatalytic activity of the coating was influenced by the nature of the interfacial oxide sandwiched between the substrate and TiO_2 coating.

Notes

(O5-S5)

TiO_2 BASED INORGANIC-ORGANIC HYBRID PHOTOCATALYSTS FOR HIGHLY SELECTIVE ALCOHOL PARTIAL OXIDATION

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ABSTRACT

Hybrid inorganic-organic nanostructured photocatalysts were synthesized by grafting a conjugated organic molecule, 4-(4-(4-hydroxyphenylimino) cyclohexa-2,5dienyl ideneamino) phenol (DIOL), and silver nanoparticles on the surface of two poorly crystallized TiO_2 samples [1]. All the three components of the catalysts were home prepared. The structure of DIOL was confirmed by FTIR and ^{1}H-NMR whereas UV-vis spectroscopy and cyclic voltammetry were carried out to investigate its electronic properties. Diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD) and Scanning electron microscopy (SEM) were used for structural and morphological characterization of the composites. The powders were tested as photocatalysts for the probe partial oxidation of 4-methoxybenzyl alcohol (4-MBA) to 4-methoxybenzaldehyde (4-MBD) [2].

In all the photocatalytic runs the powders were stable and allowed to obtain selectivity up to 86% at room temperature and pressure and under UV irradiation. This figure is the highest ever obtained for alcohol partial oxidation in aqueous media in the presence of a TiO_2 based catalyst. The present work results from opportune tailoring surface and electronic properties of the catalyst in order to obtain materials designed for specific synthetic reactions as the alcohol partial oxidation. The method is general and opens the route to fabrication of photocatalytic composites based on TiO_2 functionalized with shuttle organic molecules and metal nanoparticles for a variety of redox reactions.

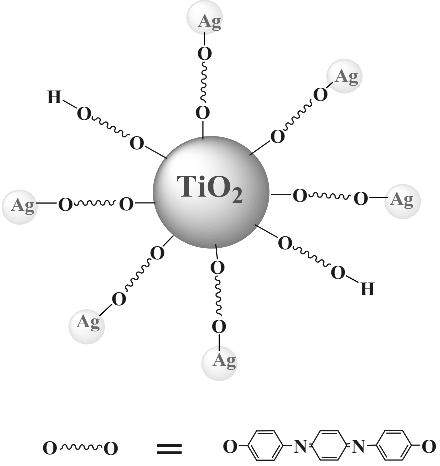

Figure 2: Schematic representation of a nanostructured hybrid TiO_2-based catalyst used for the selective partial oxidation of 4-methoxybenzyl alcohol to 4-methoxybenzaldehyde.

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Notes

(O6-S5)

TUNING THE PHOTOCHEMICAL ACTIVITY OF CARBON NANOPARTICLES: NANOCONFINEMENT AND SURFACE CHEMISTRY

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ABSTRACT

After the first studies in the 70's reporting the performance of zinc and titanium oxides to decompose cyanides in solution [1,2], the interest on semiconductors photocatalysis for the degradation of pollutants has become very popular. Triggered by the low photonic efficiency of most semiconductors, efforts are concentrated in exploring new photoactive materials with improved optical features and quantum yields.

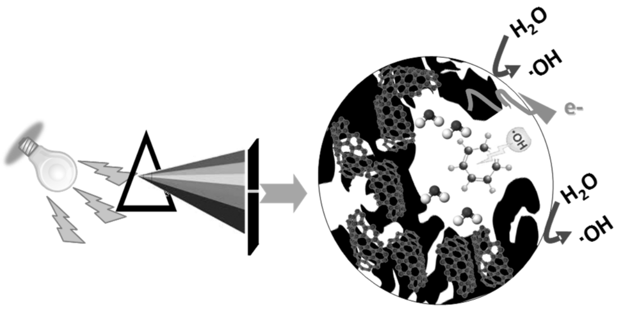

Figure1. Schematic representation of the experimental set-up used for exploring the photochemical activity of nanoporous carbons.

Our recent and pioneering research has demonstrated the photochemical activity of semiconductor-free nanoporous carbons under different irradiation conditions, demonstrating their ability to photogenerate radical oxygen species in aqueous environments [3-6]. This has opened new perspectives in the field of applied photochemistry based on carbon materials covering environmental remediation, water splitting, enhanced adsorption/oxidation, or photoluminescence [7,8]. Despite the rising interest in the field, there is still a multitude of fundamental questions that are worth investigating towards the understanding of the underlying mechanisms leading to the conversion of light into a chemical reaction to exploit the potential applications of the light-responsive carbons in different fields.

Aiming at throwing some light on the topic, we herein provide an overview on the effect of the surface composition of nanoporous carbons on the photochemical reactions hosted inside the nanopores. By combining catalytic, spectroscopic and photoelectrochemical tools, we show the dependence of the photochemical response in the confined pore space with the surface functionalization of the carbon matrix, choosing the photooxidation of phenol and the photochemical splitting of water as model reactions. Our results show that the conversion of light inside the porous network of nanoporous carbons depends on the porosity, the surface functionalization and the presence of photorreactive sites that lead to the photogeneration of charge carriers that can be effectively used in chemical reactions. The presence of a well developed porosity is essential to obtain high conversion in the constrained pore space, distinguishing low cost nanoporous carbons from graphene, carbon nanotubes or other nanostructured carbon materials. Regarding functionalization, the decoration of the nanoporous carbon surface with O-containing groups caused a decrease in the photooxidation of phenol inside the pores; however conversions were still higher in the confined pore space of the functionalized carbons than in solution

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Notes

Session 6 (S6)

Nanoparticles, films & health: safety and toxicity

(KN-S6)

NANOTECHNOLOGY IN MEDICAL DEVICES: HORIZON SCAN, RISK ASSESSMENT AND REGULATORY DEVELOPMENTS

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ABSTRACT

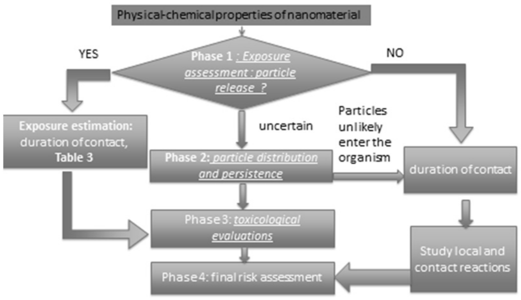
Innovative nanotechnologies are increasingly used in medical applications and are expected to have a major impact on healthcare in the future. These nanotechnology enabled medical innovations relate to both medicinal products and medical devices. Nanotechnology applications in the field of medical devices, also referred to as "nanomedical devices", span a wide range of very diverse products, technologies and application areas. Also a number of innovations in clinical chemistry laboratories are enabled by nanotechnologies. Nanomedical devices can involve the use of nanomaterials, however, nanotechnologies also enable innovative devices without using nanomaterials, for example by applying nano-electronics or lab-on-a-chip technologies. The intended use of nanomedical devices can be in the context of therapy, diagnosis, monitoring and/or prevention of disease. All medical disciplines are benefiting from nanomedical devices, especially orthopaedics, dentistry, oncology, and cardiology.

The use of nanomaterials themselves in medical devices poses a particular challenge for the safety evaluation and risk assessment of these medical devices as the specific character of the nanomaterial used should be taken into consideration. Nanomedical devices can be non-invasive or invasive, resulting in potential contact with any kind of tissue. It is important to have clear insights into the state of affairs with regard to the availability of nanomedical devices and their specific benefits and risks, not only for regulators and industry, but also for physicians and pharmacists.

A horizon scan was performed to identify nanomedical devices that are currently available on the market or under evaluation in clinical studies. In addition, we have analyzed the most promising research developments, potentially leading to products in the future. A variety of data sources was explored, including a search of scientific literature and clinical trial registries, analysis of governmental databases (FDA and Health Canada), patent analysis and commercial market reports.

Furthermore, the various aspects of safety evaluation and risk assessment of medical devices containing nanomaterials were addressed, based on the Scientific Opinion "Guidance on the Determination of Potential Health Effects of Nanomaterials Used in Medical Devices", published in January 2015 by the European Commission's Scientific Committee on Newly Identified Health Risks (SCENIHR). SCENIHR recommends a phased approach for evaluating the risk of the use of nanomaterials in medical devices based on potential release and characteristics of the nanomaterials, in order to avoid unnecessary testing. The phases cover particle release (phase 1), particle distribution and persistence (phase 2), hazard assessment (toxicological evaluations) (phase 3), risk characterisation/risk assessment (phase 4). See Figure for a graphical representation of this phased approach.

Finally, an overview of current developments in regulation and standards for medical devices with relevance for the application of nanotechnologies is provided. For example within the ISO 10993 series for the biological evaluation of medical devices a guidance document is currently under development entitled "ISO/TR 10993-22 Biological evaluation of medical devices – Part 22: Guidance on nanomateials".



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Notes

(O1-S6)

BIO-ACCUMULATION OF TiO_2 NANOPARTICLES IN CAENORHABDITIS ELEGANS: AN IN-VIVO MODEL FOR TOXICITY ANALYSIS

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ABSTRACT

Titanium dioxide (TiO_2) represents one of the most versatile and economic semiconductor materials and it is widely used in form of nanoparticles (NPs) for a variety applications such as dye sensitized solar cells, biomedical devices and photocatalysis. Besides, TiO in general is commonly used also in a lot of food products and personal care stuffs. The recent in-vivo results regarding TiO_2 toxicity [1, 2] urged the scientific community to be questioned about TiO_2 hazardness and its dependence on the shape and size of particles. Therefore, the availability of certified reference materials becomes crucial in this context. The standardization of engineered shape and size of TiO2 NPs represents the main goal of the European FP7 project SETNanoMetro. [3]

In order to provide robust metrology tools in toxicity analysis, the bio-accumulation of TiO_2 NPs reference materials with known shape and composition (Pure Anatase structure) was evaluated using the nematode *C. elegans* as model organism. To this end, *C. elegans* were fed with three different types of TiO_2 NPs: i) commercial TiO_2 (Sigma Aldrich, 25 nm sized, undefined shape, 0.2 g/l); ii) home-synthetized TiO_2 NPs synthesis suspension (50 nm bipyramidal shape, 49 nm Hydrodynamic Diameter 0.2 g/l); and iii) home-synthetized TiO_2 NPs suspension from powder (50 nm primary NPs, bipyramidal shape, 100 nm Hydrodynamic Diameter, 0.2 g/l) [4]. Preliminary studies devoted to determine the shape and size of different TiO_2 NPs were conducted using Dynamic Light Scattering (DLS) for NPs size distribution and Scanning Electron Microscopy in Transmission mode (T-SEM) for NPs shape. Moreover, Raman spectroscopy was exploited for NPs analysis because of the possibility of characterizing TiO_2 nanostructures according to their specific Raman fingerprint. The typical Raman spectrum of TiO_2 is shown in figure 1a. In particular in-vivo Raman Imaging analysis was performed on worms fed TiO_2 in order to attest the bio-accumulation of the NPs inside the body. Preliminary results regarding localization of TiO_2 NPs using Raman imaging technique are shown in figure 1b. NPs were detected along the digestive system of the worm in form of agglomerates as can be observed in figure 1c. Also confocal Raman depth profile on a TiO_2 aggregate was performed in order to obtain a 3D imaging and to attest that TiO_2 NPs were effectively inside of the worm' body and not deposited out of it.

Contextually toxicity tests of TiO_2 NPs are being performed to determine the potential toxicity of TiO_2 nanoparticles on *C. elegans*.

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Notes

(O2-S6)

CHICK MODELS FOR IN VIVO SCREENING OF NANO-SIZED TiO_2 PARTICLES AND OTHER BIOMATERIAL NANOPARTICLES

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ABSTRACT

The chorioallantoic membrane (CAM) of the developing domestic chicken (*Gallus gallus*) egg is well-known as a simple, cheap and rapid assay, of low ethical concern, for evaluating the angiogenic capacity of drugs and materials [1-3]. In recent years, the chicken egg system has also attracted interest as the basis for various models which can screen other physiological responses to biomaterials [4-9]. These models fit in between simplified cell culture experiments and more complex animal models as useful intermediate methods for determining tissue response to materials, and can be used to reduce the number of animal experiments required. All the chick models offer the same simplicity, rapidity, easy visualisation, low cost and low ethical concern as the CAM assay. The size, speed and easy availability of the model make it suitable for relatively large-scale screening. The tissue response to implanted materials can also be studied without the complication of an immune response, as the developing chick embryo is largely immuno-incompetent up to day 15 post-fertilisation [1,4], and any inflammatory responses observed are both similar to the mammalian response [5] and can be linked to more significant responses in mature animals [6,7].

Assays available in the chick system for biomaterials investigation include early blood islands formation (angiogenesis), yolk sac membrane assay (angiogenesis, inflammatory response and biocompatibility), CAM assay (angiogenesis, inflammatory response, fibrosis and biocompatibility), chick limb grafts (angiogenesis, biocompatibility, inflammatory response, toxicity, skeletal development), and *ex vivo* chick long bone and limb bud models (skeletal development) [1-11]. The assays are sensitive to soluble factors released from test materials as well as material chemical composition and surface properties [2,5,6,9]. The utility and applicability of these assays to systematic investigation of the physiological properties and behaviour of nano-sized TiO_2 coatings and TiO_2 nanoparticles will be discussed, with comparison to other biomaterials.

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Notes

(O3-S6)

NANOTOXICOLOGICAL ASSESSMENT OF SHAPE-ENGINEERED TITANIUM DIOXIDE NANOPARTICLES

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ABSTRACT

Nanoparticles have gained tremendous importance in various technological and medical applications but these developments have also raised concerns about human health risks. In the project SETNanoMetro the nanosafety aspects of highly-defined TiO_2 nanoparticles (p25, PC105, SX001 and UT001) are evaluated through in vitro toxicological testing in human type II alveolar epithelial cell line A549 and human colon epithelial cell line Caco-2, as inhalation and ingestion are considered to represent the most relevant uptake routes of nanoparticles. The pro-inflammatory potential of TiO_2 nanoparticles is specified additionally by testing lung alveolar macrophages, since they have an important role as regulator of the early immune response.

Metabolic activity analysis, evaluated by WST-1 assay revealed marked time-, concentration- and cell type-dependent differences in effects among the various TiO_2 powders. Also, the different powders have shown different hazard potential which might be related to the specific physico-chemical characteristics. So far however, all tested TiO_2 samples were clearly less toxic than SiO_2 nanoparticles that were used as reference material. In initial experiments to address the pro-inflammatory and oxidative stress potential, the pro-inflammatory cytokines interleukin (IL)-1β, IL-8 and IL-18 as well as the oxidative stress markers heme oxygenase (HO-1) and inducible nitric oxide synthase (iNOS) were evaluated on the mRNA level. The HO-1 expression level was significantly increased in rat alveolar macrophages (NR8383 cells) after treatment with three out of the four tested TiO_2 nanoparticles (SX001 was negative). Taken together our findings provide further support on the importance of the physico-chemical characteristics in the toxic and pro-inflammatory effects of TiO_2 nanoparticles. The inclusion of currently developed and highly-characterised TiO_2 nanoparticles in upcoming investigations will allow for a more precise evaluation of the role of subtle shape- and surface structure changes for this type of nanomaterial.

Acknowledgements: The SetNanoMetro is supported by funding under the Seventh Research Framework Programme of the European Union. Specific types of TiO_2 particles were provided by Solaronix (Switzerland) and the University of Torino (Italy). Commercial TiO_2 nanoparticles were kindly provided by Evonik and Cristal.

Notes

(O4-S6)

NEW MAGNETIC BIO-RESORBABLE NANOSYSTEMS AS A SMART TOOL FOR ADVANCED CELL THERAPY

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ABSTRACT

Very recently a new superparamagnetic, bioactive and bioresorbable apatite nanophase (Fe-HA) was developed, through controlled substitution of Ca^{2+} ions with $Fe^{2+/3+}$ ions in the Fe-HA lattice, in specific and defined ratios. The superparamagnetism of Fe-HA is an intrinsic property of the new apatite phase that makes it very promising for advanced applications in regenerative medicine and theranostics. In particular, superparamagnetic nanoparticles offer several opportunities in nanomedicine, and magnetic cell targeting is considered as extremely promising for the translation of cell-based therapies from the laboratory to clinical studies.

Magnetically-labeled cells can be injected in the body and driven by a static magnetic field to a target site where they can exert their specific role. Indeed, a main concern related to the use of currently available superparamagnetic iron oxide nanoparticles (SPION) is their cytotoxicity and progressive accumulation in the body, thus giving long-term harmful effects. The superparamagnetism of Fe-HA is an intrinsic property of the apatite phase and no traces of cytotoxic iron oxides such as magnetite were detected. The safety, biocompatibility and regenerative potential of Fe-HA nanophase, by means of enhanced osteogenic ability, have been demonstrated by cell-based tests.

Therefore, the new biocompatible and bioresorbable magnetic Fe-HA nanoparticles have potential to replace SPION for a variety of breakthrough applications in regenerative medicine and theranostics. In particular, new guiding systems for cells can be established by enabling selective internalization of Fe-HA nanoparticles by mesenchymal stem cells that can be injected and moved to the implant site by external magnetic driving. In vitro analysis demonstrated that this approach is suitable to bring cells into inner, selected areas of hybrid scaffolds with complex composition and morphology designed for bone and osteochondral regeneration. This would greatly enhance regeneration of critical size defects for which no acceptable solutions are available to date. This work demonstrated the promising opportunities of FeHA nanoparticles in cell labeling due to the unique features of fast degradation and very low iron amount of FeHA NPs compared to SPION. This approach could be simply transferred to different cell types and, also, they could be used as magnetic carrier of drugs, growth factors, miRNA, etc., thus opening wider perspectives in nanomedicine.

Notes

(O5-S6)

THE ROLE OF ILLUMINATION IN THE HAZARD ASSESSMENT OF NANO-TiO_2

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ABSTRACT

TiO_2 powders are contained in different kinds of industrial products including paints, self-cleaning glasses but also as a food, cosmetics and pharmaceutical products [1-2]. In the nanometric form TiO_2 is mainly used as UV filter. This material is also largely studied because of its photocatalytic activity [3-4]. When TiO_2 particles are irradiated by UV light charge separation takes place in the bulk producing both electrons (e^-) and holes (h^+). Surface localized electrons and holes promote reductive and oxidative reactions respectively. This reactivity, in aqueous media, produces a large amount of reactive oxygen species (ROS) which are able to depredate organic compounds [5]. Therefore, this material can be used as an active agent for the remediation of polluted water, for the production of self-cleaning coatings or as antibacterial agent [6].

Titania nanoparticles have been found to elicit toxic responses in vivo and in vitro systems [7,8] and it is classified by IARC in group 2B (possibly carcinogenic to humans) (IARC 2006). Several studies reports that the toxic effects are largely modulated by physico-chemical properties of TiO_2 such as specific surface area and crystallinity [8,9]. The photo-generated ROS (hydroxyl radicals HO°, superoxide radicals $O_2^{-\circ}$ and singlet oxygen $^1O_2$) which in low concentration have important physiological functions in cells, in high amount are highly toxic to living organisms. In fact they have been found to play a key role in the acute cytotoxic and genotoxic effects elicited by sun-light activated TiO_2 [10]. Conversely, the role of such species in the dark, that at the end is the condition that really simulate the “in vivo” conditions, is still under debate.

In the present study, the reactivity of a set of TiO_2 samples having different physico-chemical properties has been studied in light and dark conditions by means of electronic paramagnetic resonance (EPR) by using a set of different probes and experimental conditions to identify the primary ROS generated (HO°, $O_2^{-\circ}$, $^1O_2$) . The results have been compared with those obtained by using a dye commonly used to assess the photo-efficiency of TiO_2 powders. The ability of the nano-powders to induce oxidative damage has been also evaluated by measuring the degradation of two representative biomolecules, i.e linolic acid and 2-deoxyribose. The results show that illumination modulates the surface reactivity of TiO_2 depending upon the type of materials and therefore underline the importance of a controlled illumination during toxicological testing.

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Notes

(O6-S6)

CONTROL OF NANOTITANIA SURFACE PHOTOREACTIVITY TO ADDRESS SAFETY ISSUES

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ABSTRACT

The potential risk of health damage to humans caused by the exposure to nanometric-sized particles is, nowadays, a very current topic. In particular, titanium dioxide (TiO_2) nanoparticles (NPs) are extensively studied since they are widely used in industry for several applications ranging from sunscreens, pigments and construction materials to solar cells [1-5]. The biological effects depend mainly on their surface chemistry (phase composition, structural defects, impurities) and nanostructure (morphology, size). The biological activity of TiO_2 is enhanced by UV light exposure due to TiO_2 photoactivation generating radicals such as $^{\bullet}OH$ and $O^{2\bullet -}$ and other reactive oxygen species (ROS), able to react with a wide range of organic molecules [6,7]. In order to control and harmonize the biological activity of TiO_2 NPs the development of particles coating with inert inorganic materials, as risk remediation strategy based on a “safety by molecular design” approach, was studied. Silica was selected as inorganic coating thanks to its known chemical inertia, biocompatibility, low toxicity and ability to create mesoporous structure [8]. The present work is addressed to the production and characterization of SiO_2-coatings on TiO_2 NPs, dispersed in aqueous solutions (commercial nanosols) with the aim to manage their potential risk. A colloidal approach, based on electrostatic attraction between opposite surface charges (heterocoagulation), was followed. Physicochemical properties such as zeta potential, particle-size distribution, morphology and hydrophilicity (by adsorption microcalorimetry) of the samples produced with different SiO_2:TiO_2 weight ratios were measured and compared with photocatalytic properties. In particular the production of free radicals was investigated with different techniques, providing useful information for the evaluation of the photoreactivity and of potentially hazardous effects. Three experimental protocols were employed: a recently developed electrochemical technique to determine hydroxyl radicals and two well-known methods, namely trapping of •OH radicals by salicylic acid and degradation of Rhodamine B. A comparative analysis between the results obtained by three methods was made in order to improve the knowledge of the photocatalytic mechanism in which free radicals are involved [9]. The research leading to this commentary has received funding through the project “SANOWORK” (FP7-NMP4-SL-2011-280716).

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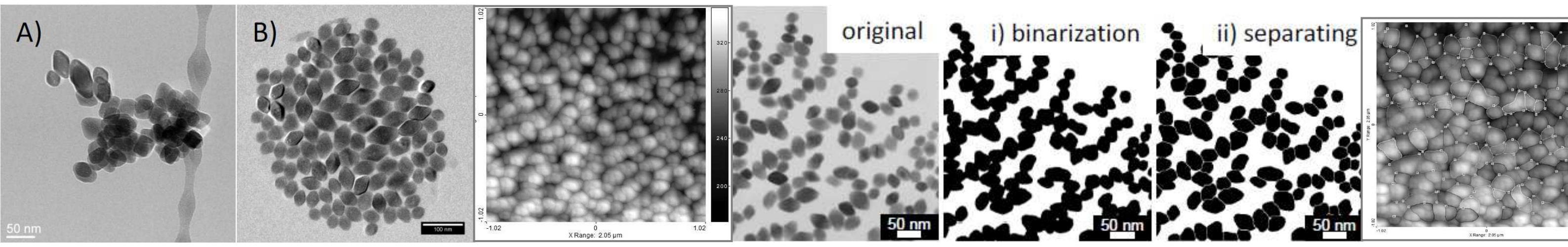

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