# 1. Publishable executive summary

## 1.1 Project Objectives and contractors involved

Based on the state-of-the-art in the relevant fields, the main objectives of the project are:

a) To achieve **self-organized $TiO_2$ nanotubes** with a similar degree of order as with porous $Al_2O_3$ and Si. This part of the work is mainly carried out at the coordinators' laboratory and is performed constantly over the duration of the project. It has been possible to generate porosity in many different valve metals so far [1-7] which is a very promising precondition for this part of the project. The very interesting results in this area have shown that there is a broad range of systems that can be treated to generate porous structures and that, depending on the conditions of anodizing, various pore dimensions, orientations, conformations and morphologies can be obtained. A further important aspect is the influence of annealing procedures which is investigated in parallel. Overall, there will be more significant effort put into the art of creating new porous structures under different conditions.

b) The **properties** of all the different systems achieved in (a) are investigated with surface analytical techniques being SEM, XPS, AES and ToF-SIMS.

c) The key **mechanisms** leading to self-ordering (field effects, chemical effects, stress induced effects, etc.) have to be identified and investigated in order to understand better the driving forces for pore development, continued growth, and self-ordering. The investigations related to this milestone are performed at UM and at FAU, particularly with TEM and the surface analytical techniques mentioned in (b) and later work packages. These detailed studies are carried out on every new system that shows tube growth under certain conditions. This objective is therefore accompanying every system investigated and is an important part of the project throughout its overall duration.

d) The possibility to exploit the self-organized $TiO_2$ nanotubes with focus on solar-energy conversion (dye-sensitized solar cell) is addressed. The effect of doping and dye sensitization will be investigated in detail. The properties of self-organized $TiO_2$ nanotube layers and their performance, compared with currently used nanostructured systems produced by $TiO_2$ nanoparticle sintering, is determined in this step. The research related to this milestone is mainly carried out in Greece by Dr. P. Falaras's group at the NCSRD as they have the highest state of knowledge in this area. Nonetheless, researchers will be exchanged between the institutes in order to guarantee the exchange of knowledge and ideas. NCSRD provides the synthesis of new sensitizers presenting broad and intense metal to ligand charge transfer (MLCT) absorption bands in the visible like Ru(II) complexes of bipyridine (bipy), terpyridine (terpy), phenanthroline and related ligands bearing carboxylic or phosphonic acid functional groups and their efficient incorporation (and optimisation) in dye-sensitised photoelectrochemical solar cells, having a solid-state structure and using polymer based redox electrolytes. Surface chemical modification of the Ti-Nanotubes by noble metal

deposition and N, S, P doping is performed for direct application in photocatalytic processes, including fabrication, modeling, and evaluation of photocatalytic reactors for efficient photodegradation of water (azo-dyes) and air pollutants (volatile organic compounds, VOCs). Eventually, superhydrophylic surfaces with self-cleaning and anti-fogging properties will be developed.
This objective is split into two main parts: first, fundamental research on the newly developed systems from objectives a), b) and c) and their comparison in terms of the photo-response and second, the development of new photo-active nanotube-systems (ideas are based on the results obtained with the already investigated nanotube arrays) which in turn will be produced at the FAU (a).

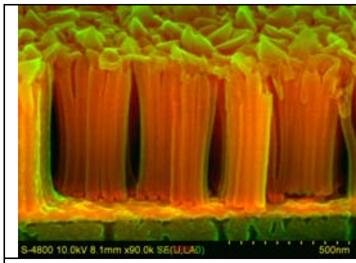
The main innovative aspect is the application of new nanotube-structures that have been produced by anodizing under different experimental conditions. The investigation methods performed in (b) and (c) will give a clear insight into the mechanisms of pore generation and growth and the investigations and application in (d) will reveal aspects that are important for the technological improvement of the produced nanotubes. The different systems can be classified in terms of their technological value and new ideas for improvement of the systems can be developed and optimized simultaneously.

## Co-ordinator contact details:

**Contact Person:**
Dr. Julia Kunze
**Organisation:**
University of Erlangen-Nuremberg
Department of Materials Science and Engineering
Chair for Surface Science and Corrosion (LKO)
Martensstr. 7
D-91058 Erlangen
Germany
Tel: +49 9131 85 27580
Fax: +49 9131 85 27582
E-mail: kunze@ww.uni-erlangen.de
**Project Website:** http://www.ist-world.org/

## 1.2 Major achievements during the reporting period

The level of control over the $TiO_2$ nanotubes has been increased tremendously so that the geometry (diameter and length) can be perfectly tailored. All possible parameters that influence the morphology of the nanotubes have been scanned and are permanently controlled with the respective surface analysis methods employed in WP2. Thus, WP1 and WP2 work perfectly complementary and bring the project closer to the overall objectives (a) and (b), being the achievement of **self-organized $TiO_2$ nanotubes** with a similar degree of order as with porous $Al_2O_3$ and Si and the investigation of the **properties** of all the different nanotubular systems.



SE/BSE image of $TiO_2$ nanotubes with one W marker layer.

For the mechanistic studies on the nanotube formation a very good summary of all the essential literature related to self-organization and growth has been written. This will help for the further interpretation of the data. $TiO_2$ nanotubes have been grown on sputtered Ti films employing glycerol electrolyte at FAU which is a very important success in the project. **Mechanistic studies** based on anodization of sputtered films containing W marker layers have been brought to perfection which is an excellent achievement for the overall objective (c). The numeric simulations performed by FAU give very fruitful complementary information for the interpretation of the formation mechanism of $TiO_2$ nanotubes. Those theoretical findings could be supported by thorough SEM and ToF-SIMS studies at FAU and by GDOES, TEM, EELS and XDS measurements at the UM.

The overall objective (d), the possibility to exploit the self-organized $TiO_2$ nanotubes with focus on solar-energy conversion (dye-sensitized solar cell) has been addressed with great success as well. The effect of doping and dye sensitization is being investigated in detail and brings new insights into the system. The properties of self-organized $TiO_2$ nanotube layers and their performance, compared with currently used nanostructured systems produced by $TiO_2$ nanoparticle sintering is being determined and first results on 'Efficient solar energy conversion using $TiO_2$ nanotubes produced by rapid breakdown anodization' have already been summarized in a paper. These results made use of one of the systems explored in WP1 and 2 that gives a really high photoresponse. The newest studies reveal an overall conversion efficiency of 4.29% when measured in a real solar cell set-up. Those findings need to be confirmed and will be published in the near future. On the other hand, another system explored in WP1 and 2 led to efficiencies as high as 0.76% (with 20 $\mu$m long nanotubes) under back-side illumination. These tubes when deposited on conductive glass increased their efficiencies up to ~3%.

Chemical modification of the $TiO_2$ nanotubes by noble metal (Ag, Au) and anionic (N, S, P) doping has been implemented by soft chemical methods (Ag, N, S) as well as ion-implantation (P) and pulsed laser deposition (Au) on $TiO_2$ nanotubes of 0.5 and 1.0 $\mu$m length, resulting systematically in the enhancement of the photocatalytic response over that of pristine samples. No appreciable photocatalytic activity could be detected in the visible range. Most importantly, surface functionalization of $TiO_2$ nanotube arrays by dextrin coated iron oxide nanoparticles has been demonstrated to lead to a hybrid magnetic/$TiO_2$ oxide nanocomposite, which provides a promising means to enhance the photocatalytic activity and to vary the surface wettability of the $TiO_2$ nanotubes, while adding a magnetic character brought up by the iron oxide component. These results are summarized in a joint paper that has just been submitted.

## 1.3 Expected end results, intentions for use and impact

- Design and processing of new systems consisting of Ti or other valve-metals with enhanced properties for their application and use in the field of nanotechnology.
- Accumulation of new knowledge by fundamental research on the $TiO_2$ nanotube structures, including self-organization effects together with their mechanisms.
- Direct investigation of the technological importance of the relevant systems; potential for economic, environmentally-safe production of new generation solar-cells with significant efficiency and cost-benefits over existing technologies.

## 1.4 Main elements of publishable results

The following exploitable results have been achieved in the first phase of the project so far:

1.) Efficient Solar Energy Conversion by $TiO_2$ Nanotubes - a Comparison:

- A certain type of $TiO_2$ nanotubes that is produced in chloride containing electrolytes shows very high solar cell efficiency. This system will be investigated in all detail for its application in a solar cell.
- Solar-energy conversion applications possible.
- The findings are at that stage of development of a fundamental nature.
- I-V characteristics on dye-sensitized solar cells are to be performed at NCSRD.

2.) Ag doping of $TiO_2$ nanotubes:

- $TiO_2$ nanotubes have been doped with Ag nanoparticles.
- The Ag-modified nanotube arrays presented an enhanced photocatalytic activity.
- High surface wettability was evidenced.
- Solar-energy conversion applications possible.
- The findings are at that stage of development of a fundamental nature.
- SEM and XPS measurements (performed at FAU) have identified the presence of Ag as a mixture of oxides.
- BSE images have to be taken at UM.

3.) Fe doping of $TiO_2$ nanotubes:

- $TiO_2$ nanotubes have been doped with Fe nanoparticles to produce nanotube arrays with enhanced photocatalytic activity.
- Solar-energy conversion applications possible.
- The findings are at that stage of development of a fundamental nature.
- XPS measurements have been performed at FAU
- Photo efficiency measurements have been confirmed at NCSRD.

4.) Mechanistic studies

- $TiO_2$ nanotubes have been created on sputtered Ti substrates which contained either a single layer or multiple layers of W markers.
- TEM and High Resolution TEM has been carried out
- Multiple layers of W markers revealed a varying expansion rate during the initial stages of pore generation.
- RBS has further confirmed results found with the TEM and provided further details about the efficiencies with which the oxides are produced.

## References

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