1. Publishable final activity report

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** (NTs) 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, in particular SEM, XPS, AES, RBS, NRA, MEIS 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 relevant to 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) gave a clear insight into the mechanisms of pore generation and growth and the investigations and application in (d) revealed aspects that are important for the technological improvement of the produced nanotubes. The different systems have been classified in terms of their technological value and new ideas for improvement of the systems can be developed and optimized simultaneously.

1.2 Major achievements during the full duration of the project

The level of control over the TiO_2 nanotubes (NTs) has been increased tremendously so that the geometry (diameter and length) can be precisely tailored. The key parameters that influence the morphology of the nanotubes have been scanned and optimized, assisted by the respective surface analysis methods employed in WP2. Thus, WP1 and WP2 were entirely complementary and ensured the achievement of the overall objectives (a) and (b), being the generation 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.

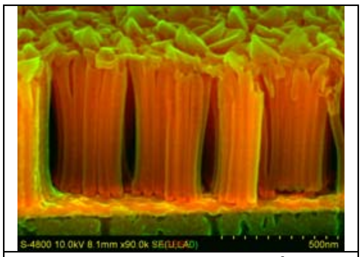

Fig. 1: SE/BSE image of TiO_2 nanotubes with one W marker layer.

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 helped for the further interpretation of the data. TiO_2 nanotubes have been grown on sputtered Ti films employing glycerol electrolyte at FAU, which was 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 was an excellent achievement for the overall objective (c) [8]. The numeric simulations performed by FAU gave very fruitful complementary information for the interpretation of the formation mechanism of TiO_2 nanotubes [9]. Those theoretical findings were supported by thorough SEM and ToF-SIMS studies at FAU and by GDOES, TEM, EELS and XDS measurements at the UM.

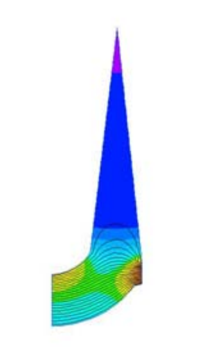

Fig. 2: Schematic diagram of the simulation of an electric field within a nanotube generated by a finite element analysis program.

TiO_2 nanotubes have been grown on sputtered Ti films employing glycerol electrolyte at FAU. Using TEM, HRTEM, EDX, EELS, RBS and NRA, it was demonstrated that the barrier type film and the walls of the nanotubes are locally enriched with fluoride and carbon, incorporated from the electrolyte. Anodized multi-layered specimens proved that the expansion ratio of the nanotubes varies in the early stages of film development. From these results, it was possible to give detailed explanations of several mechanisms involved in the growth of TiO_2 nanotubes. Carbon enrichment from the glycerol electrolyte occurs on the inside of the nanotubes. The enrichment produces two distinct layers within the walls and the barrier layer of the nanotubes. The thickness of these layers remains at a constant ratio during the steady state growth of the nanotubes. The consistency of the thickness of the layers is due to the flow of the titania due to the pressure gradients caused by electrostriction and the pressure generated by the production of new oxide.

The mechanistic studies on the nanotube formation revealed that TiO_2 nanotube growth can be explained by a flow mechanism; this shows close similarities to the mechanism used for the explanation of alumina nanopores. However, studies on the efficiency of tube growth and on the expansion factor of the nanotubular oxide revealed that the mechanism is more complex than that of alumina pores – the growth is characterized by a combination of dissolution and flow [10]. This complex mechanism is being investigated further, using various methods, and new insights have been won. The initial stages of tube formation have been investigated using sputter deposited titanium thin films. A photoresist-masking method of thin Ti films allows the use of SEM cross-sections to obtain directly information on oxide morphology, layer thickness and metal substrate loss. Therefore, not only features of the initial growth stages, but also oxide expansion factors can be accurately determined [11]. The obtained results suggest a substantial contribution to steady state tube growth by a plastic oxide flow mechanism. Combined with RBS efficiency measurements, the method presented here allowed for facile and direct investigation of the mechanism of pore/tube formation [12].

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. The effect of doping and dye sensitization has been investigated in detail and brought new insights into the system [13-15]. The properties of self-organized TiO_2 nanotube layers and their performance, compared with currently used nanostructured systems produced by TiO_2 nanoparticle sintering has been determined. These results made use of one of the systems explored in WP1 and 2 that gives a really high photoresponse. For instance, 20 μm long nanotubes, explored in WP1 and 2, led to efficiencies as high as 1.65% under back-side illumination [14].This efficiency was increased up to 1.90 % by optimizing the cell configuration. Tubes with slightly smaller thickness (16 μm) and a diameter of 120 nm increased the efficiencies up to 2.4 % [15].

In this context, a variety of different tubes were used as substrates in order to identify the best system for a DSSC based on titania nanotubes. DSSCs based on 30 μm tubes with a mean diameter of 20-40 nm grown by a different method than ordinary self-ordering conditions, i.e. Rapid Breakdown Anodization (RBA), have shown a conversion efficiency of 0.63 % in solar cell configuration that was further increased up to 3.1 % by encapsulation of the cells.

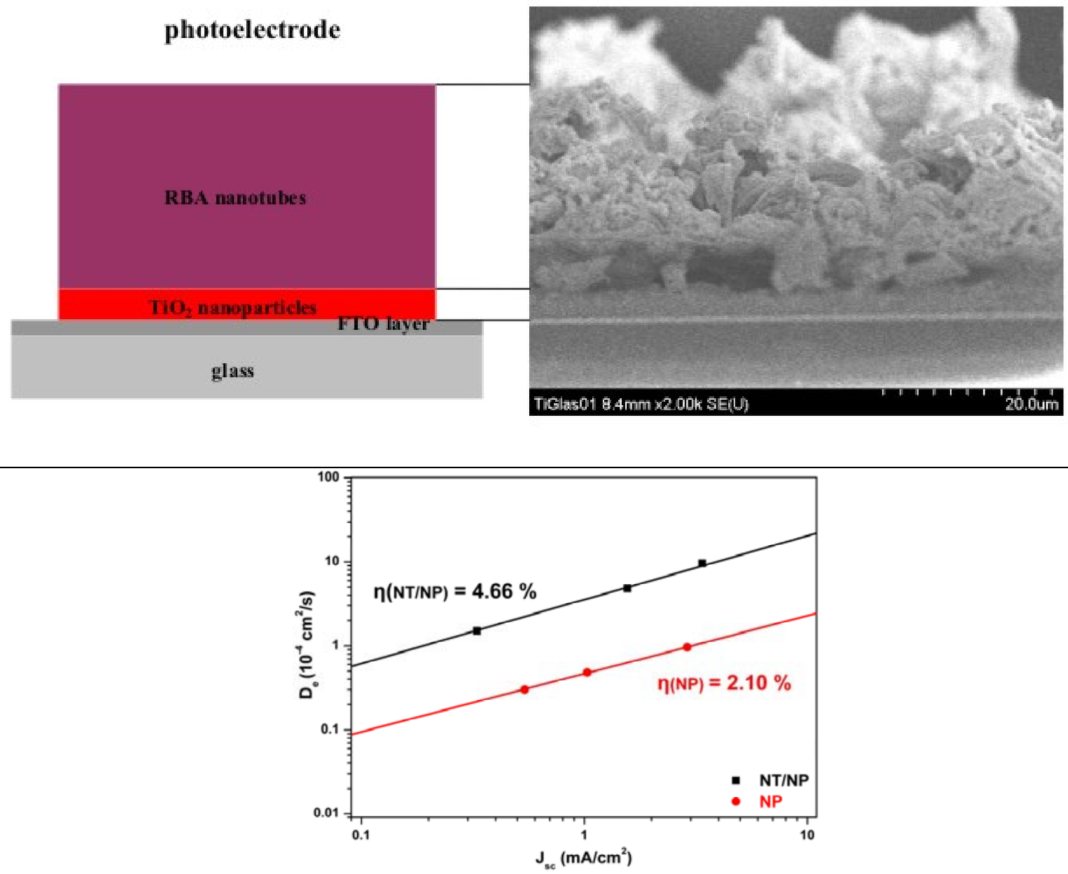

Fig. 3: (a) Schematic representation of the DSC illuminated by the photoelectrode side. The SEM cross section of TiO_2 nanotubes grown under RBA conditions and NP film deposited on conductive glass are also shown. (b) Electron diffusion coefficients derived from the IMPS diagrams with varying J_{sc} (with variation of the LED DC illumination power) are shown along with the obtained overall conversion efficiencies.

In order to avoid limitations arising from back-side illumination, the tubes were chemically lifted off the Ti-foil and fixed on a transparent conductive substrate (TCO) with a transparent nanoparticulate paste. The DSSCs constructed with ethylene glycol (EG) tubes deposited on the TCO presented efficiencies as high as 3 %, while the RBA tubes showed an efficiency of 4.7 % due to the better light harvesting and electron diffusion properties of the nanotubular membrane (Fig. 3). The use of a NT overlayer can also act as a scattering layer, being a good substitute for the standard large nanoparticles that are currently used in the DSC technology.

On the other hand, much lower efficiencies were obtained (0.3 %) by direct anodization of Ti sputtered on glass due to the limited tube thickness and the increased resistance at the TiO_2/FTO interface caused by the presence of a non-anodized Ti layer. However, this concept is very promising since galvanostatic conditions were reported for the first time here for the preparation of tubes on FTO glass.

Finally, novel composite redox electrolytes using anodic powders as fillers were prepared, leading to efficiencies up to 7.5 %, which is one of the highest efficiencies in literature for a quasi solid-state DSC using a solidified polymer electrolyte, due to improved thermal and electrochemical properties in relation to the non-filled electrolytes. We believe that this aspect will spur the scientific community to use tubes instead of nanoparticles to solidify their liquid redox systems.

Anodic TiO_2 nanotube arrays with appropriately tuned morphologies can be efficiently incorporated as an immobilized photocatalyst in liquid phase photoreactors and become highly effective in the photocatalytic removal of hazardous organics. The most efficient TiO_2 nanotubes for application in photocatalysis were identified by systematic experiments on TiO_2 NT arrays with different morphologies as well as subjected to different modifications, including surface deposition of noble metal particles, non-metals and iron-oxide nanoparticles by either soft chemical or physical (ion implantation or laser ablation) deposition techniques. Vertically oriented nanotube arrays with thickness of the order 10 μm were thus identified as the best substrate for the photocatalytic degradation of volatile organic compounds (benzene and toluene) and water pollutants (methyl orange). Surface modification of the TiO_2 nanotubes following soft chemical routes using Ag and S leads to the best results concerning both the photocatalytic efficiency as well as wetting and photo-induced superhydrophilicity that determine the self-cleaning ability of the nanotubular substrate. Furthermore, surface functionalization of the TiO_2 NT arrays by dextrin coated iron oxide (γ-Fe_2O_3) nanoparticles provides a composite vertically oriented nanostructure that exhibits high photocatalytic activity for the degradation of model pollutants at relatively low loading levels of the γ-Fe_2O_3 nanoparticles and light independent wetting properties, related to the improvement of the interfacial electron-transfer kinetics and the modification of the surface chemistry [13]. This advantageous combination of the two oxide nanostructures leads to the effective separation of photocatalytic and wetting properties that renders these nanocomposite materials very attractive for self-cleaning and for biomedical applications.

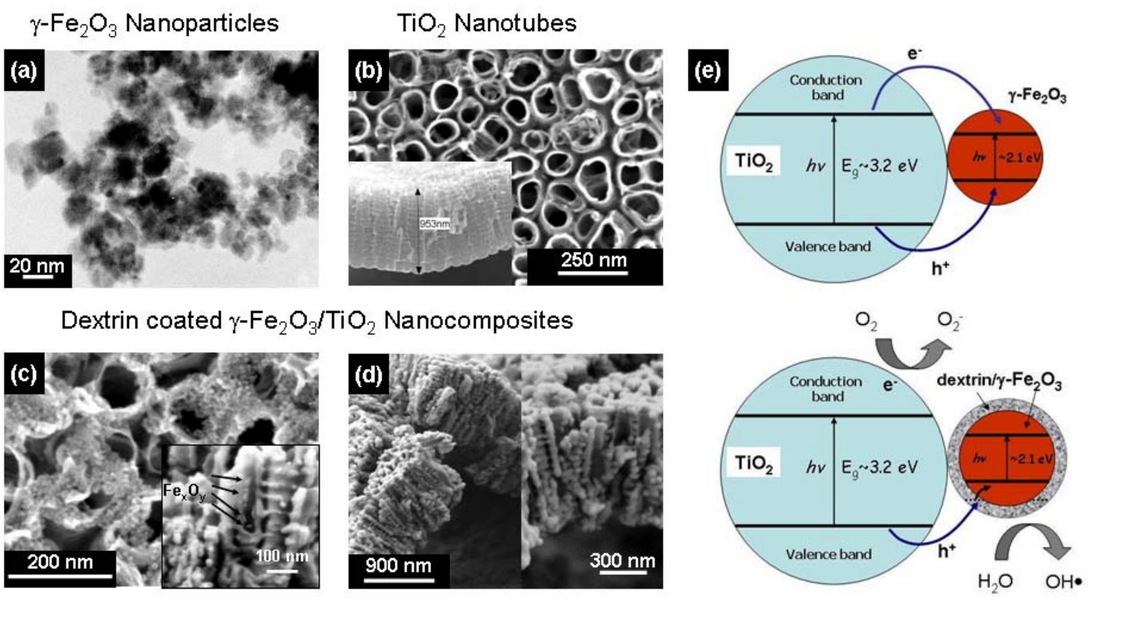

Fig. 4: (a) Low magnification HR-TEM micrograph of the γ-Fe_2O_3 nanoparticles. (b) Top and side view SEM images of the unmodified TiO_2 NTs. SEM images of the TiO_2 NTs after deposition of the iron oxide nanoparticles at (c) 5 mg/ml and (d) 10 mg/ml. (e) Schematic charge transfer mechanism between the oxide semiconductors and photocatalytic action of the nanocomposite [13].

Moreover, the photocatalytic activity of TiO_2 NT arrays for the decomposition of gas pollutants (NO_x and toluene) has been evaluated by efficient integration of appropriate size materials in a special gas phase photocatalytic reactor that was designed and developed. TiO_2 NT arrays anodized at larger scale have been thoroughly characterized by microscopic and spectroscopic techniques and have been shown to retain the structural characteristics of anodized TiO_2 nanotubes. These materials enabled efficient contact between the TiO_2 NT substrate and gas pollutants in the newly developed gas-phase photocatalytic reactor. Self-organized TiO_2 NT arrays have been found to exhibit high photodecomposition efficiency for the destruction of gas pollutants depending on the nanotubular morphology and length as well as the TiO_2 phase composition of the materials. Combination of the photocatalytic activity of TiO_2 NT arrays for the decomposition of gas pollutants, including both NO_x and VOCs, with their high performance for the photodegradation of organic pollutants from water and their photoinduced superhydrophilicity hold great promise for their application as self-cleaning photocatalytic surfaces. Innovative designs have been devised for the efficient incorporation of self-organized anodic TiO_2 NT arrays in current photocatalytic reactor technology both as an immobilized photocatalyst on the metallic Ti-foil as well as a free standing photocatalytic membrane.

1.3 Main elements of publishable results

The following exploitable results have been achieved:

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 were 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.

5.) Mechanistic studies
- TiO_2 nanotubes have been created on sputtered Ti substrates.
- The influence of the water content on nanotubular anodic titania formed in both fluoride/glycerol and fluroide ethylene glycol electrolytes has been studied.

6.) Mechanistic studies
- TiO_2 nanotubes have been created on sputtered Ti substrates.
- ‘The efficiency of nanotube formation on titanium anodized under voltage and current control in fluoride/glycerol electrolyte has been studied with various methods.
- The compositions of nanotubes have been determined by RBS and NRA to reveal the presence of fluorine and carbon contaminants of the titania.

7.) Mechanistic studies
- Initial stages of nanotube formation have been studied on Ti foils.

8.) Mechanistic studies
- TiO_2 nanotubes have been created on sputtered Ti substrates.
- Initial stages of nanotube formation have been studied on sputtered Ti substrates.
- Nanotubes have been produced on alloy substrates and investigated by TEM and ion beam analysis.

9.) Efficient Solar Energy Conversion by TiO_2 Nanotubes:
- Study on 'Dye-sensitized solar cells based on thick highly ordered TiO_2 nanotubes produced by controlled anodic oxidation in non aqueous electrolytic media'.

10.) Efficient Solar Energy Conversion by TiO_2 Nanotubes:
- Study on 'TiO2 nanotube dye-sensitized solar cells: Critical factors for conversion efficiency'.
- **REMARK:** this work is part of the Ph.D. thesis of Andrei Ghicov who is working at the FAU.

11.) Raman investigations on TiO_2 Nanotubes:
- Study on the 'Phase composition, Finite Size, Orientation and Antenna Effects of Self-Assembled Anodized TiO2 Nanotube Arrays: A Polarized micro-Raman Investigation'.

12.) Characterization studies:
- Structural and morphological properties including roughness and fractal analysis on the whole series of the Ti-nanotubes.

13.) Self-cleaning properties:
- Syperhydrophilicity and photocatalytic activity of Ti-nanotubes

2.) Photoinduced applications involving TiO_2-nanotubes:
- Gas pollutants (VOCs and NOx) photodecomposition on Ti-nanotubes.

3.) Efficient Solar Energy Conversion by TiO_2 Nanotubes: Optimization studies
- Efficient polishing of the titanium foils before anodization leads to elimination of disordered top layers, improving the morphology of the produced tubes and consequently increasing the photoconversion efficiency of DSCs.
- Different morphologies could be obtained by a dual anodization method resulting in bamboo-type tubes. These tubes presented an overall efficiency of 2.96 %.
- Decoration of 20 μm tubes with TiO_2 nanoparticles improved the efficiency from 1.9% to 3.8%.

4.) Efficient Solar Energy Conversion by TiO_2 Nanotubes: Optimization studies
- Galvanostatic tubes prepared in UM were successfully incorporated in DSCs, providing efficiencies of the order of 0.3 %.
- RBA tubes prepared under optimum conditions of anodization presented higher efficiencies (0.86 %) when sensitized by the N3 dye when replacing the standard N719 complex (0.61 % respectively). The role of the dye on the photovoltaic efficiency of DSCs-based on RBA tubes was thoroughly investigated.
- Novel nanotubular structures prepared during two-step anodization did not lead to optimization of the obtained efficiencies. Detailed

photoelectrochemical characterization (EIS, IMPS, IMVS) revealed very high values of interfacial resistance at the semiconductor's surface in contact with the electrolyte.

- The very high efficiency (4.66 %) obtained by RBA tubes transferred from the Ti-foil to glass was studied by advanced photoelectrochemical methods; it was concluded that the increased photocurrent is not only the result of higher dye loading but also comes up from improved transport properties.
- The mechanical removal of the top (disordered) loose layer on the surface of tubes resulted in improved efficiencies.

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