



**UNIVERSITY OF  
CHEMISTRY AND TECHNOLOGY  
PRAGUE**

# **New trends in photo and electro catalysis**

**Proceedings of the 8<sup>th</sup> Czech-Austrian workshop**

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EDITOR

30<sup>th</sup> November – 2<sup>nd</sup> December 2016

Hnanice, Czech Republic

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## PREFACE

Czech - Austrian workshops „New trends in photo and electro catalysis“ represent a successful series of the conferences organized jointly by the University of Chemistry and Technology, Prague and Vienna University of Technology. The first Czech – Austrian workshop was held in November 2006 in Hnanice, Czech Republic. The 2<sup>nd</sup> workshop was held in December 2008 in Telč. Then the 3<sup>rd</sup>, 4<sup>th</sup>, 5<sup>th</sup> and 6<sup>th</sup> workshops were held in Hnanice in autumns 2009, 2011, 2012 and 2013, respectively. The last, 7<sup>th</sup> Czech - Austrian workshop was held in Hnanice in spring from 25<sup>th</sup> to 27<sup>th</sup> May 2015.

The 8<sup>th</sup> Czech - Austrian workshop „New trends in photo and electro catalysis“ is held in Hnanice, Czech Republic from 30<sup>th</sup> November to 2<sup>nd</sup> December 2016. There is a small change in the organisation; Proceedings from the workshop are this time printed before the workshop.

Participants are from five Czech institutions: University of Chemistry and Technology, Prague; Jaroslav Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic; Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic; Faculty of Chemical Technology, Technical University Brno and Institute of Physics, Academy of Sciences of the Czech Republic, two Austrian institutions: Vienna University of Technology and University of Salzburg, one Slovak institution: Slovak University of Technology in Bratislava, one German institution: Friedrich-Alexander University, Erlangen and one Slovenian institution: University of Ljubljana

The objective of the workshop was, similarly as for previous years, to further intensify the exchange of experience and new ideas in the field of semiconductor photocatalysis and photoelectrochemistry, dye sensitised solar cells, electrochemically prepared self organised structures, fuel cells, electrochemical engineering and modelling of electrochemical processes. Workshop was especially useful for PhD students who could present their results at the international forum.

The positive aspect of the workshop was the participation of new PhD students from both Austrian universities in Vienna and Salzburg. Unlike last workshop, this time there are again participants from other European countries (Slovakia, Germany and Slovenia) and this shows the international aspect of the workshop. Especially due to the fact that at the time of the 8<sup>th</sup> workshop, in autumn 2016, we celebrate the 10 years anniversary in the history of Czech – Austrian workshops „New trends in photo and electro catalysis“. For the next workshops the proposed scheme will be that they will be organised in regular intervals in either autumn or spring. Therefore the next workshops are planned to be organised in Spring 2018 and Autumn 2019.

Josef Krýsa and Guenter Fafilek

## Acknowledgement

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## List of participants

### Austria

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Assoc. Prof. Dr. Guenter Fafilek  
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## Programme

Wednesday, 30<sup>th</sup> November

11.00 – 13.00 arrival

13.00 – 13.30 registration of participants

13.30 welcome talk (Josef Krýsa)

*Chair: Vlasta Brezová*

**13.40** Ladislav Kavan

Conduction Band Engineering in TiO<sub>2</sub>: Electrochemistry, Photocatalysis and Applications

**14.10** Jan Balajka, Martin Setvín, Zdeněk Jakub, Matthias Müllner, Stijn Mertens, Michael Schmid, Ulrike Diebold

Stability and Structure of TiO<sub>2</sub> Surfaces in Liquid Water

**14.25** Georg Brunauer, Guenter Fafilek

A Novel Approach in Solid Oxide Photo-Electrochemistry: Basis for Thermally Activated Solar Energy Conversion

**14.40** Hana Krýsová, Andrea Li Bassi, Ladislav Kavan

Electrochemical and Photoelectrochemical Properties of Tantalum Doped Titania Thin Films

15.00 – 15.45 coffee break

*Chair: Guenter Fafilek*

**15.45** Vlasta Brezová, Zuzana Barbieriková, Dana Dvoranová

EPR Spectroscopy for the Analysis of Paramagnetic Species in the Titania-Based Photocatalytic Systems

**16.15** Florian Kraushofer, Zdeněk Jakub, Magdalena Bichler, Ulrike Diebold, Peter Blaha, Gareth Parkinson

Atomic Scale Studies of the Hematite (012) Surface

**16.30** Martin Zlámal, Šárka Paušová, Štěpán Kment, Zdeněk Hubička, Josef Krýsa

Preparation and Photoelectrochemical Properties of Mixed Hematite-Titanium Dioxide Transparent Nanotubular Layers

**16.50** Selda Ozkan, Nhat Truong Nguyen, Anca Mazare, Isotta Cerri, Patrik Schmuki

Key Parameters for Controlled Spacing of Anodic TiO<sub>2</sub> Nanotubes

**17.05** JeongEun Yoo, Patrik Schmuki

Photocatalytic H<sub>2</sub> Generation Using Dewetted Noble Metal Decorated TiO<sub>2</sub> Nanotubes: Optimized Dewetting and Oxide Crystallization by a Multiple Annealing Process

**17.20** Vit Kašpárek, Krisztina Kocsis, Thomas Berger, Jaroslav Cihlar, Oliver Diwald

Colloidal Nanoparticle Processing and Water Splitting Catalyst Preparation

17.35 end of the session

19.30 dinner



## Thursday, 1<sup>st</sup> December

*Chair: Ladislav Kavan*

**9.00** Dana Dvoranová, Milan Mazúr, Zuzana Barbieriková, Vlasta Brezová, Tatiana Giannakopoulou, Christos Trapalis

Photoinduced Reactions of Composite g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> Photocatalysts

**9.20** Eva Pližingrová, Mariana Klementová, Petr Bezdička, Jaroslav Boháček, Zuzana Barbieriková, Dana Dvoranová, Milan Mazúr, Vlasta Brezová, Jan Šubrt, Josef Krýsa  
Preparation, Characterization and Photocatalytic Activity of Modified 2D-Titanium Dioxide Nanosheets

**9.35** Zuzana Barbieriková, Dana Dvoranová, Vlasta Brezová, Eva Pližingrová, Jan Šubrt  
EPR Study of Doped Lamellar Anatase Nanoparticles

**9.55** Matthias Niedermaier, Markus Schuhmann, Korbinian Aicher, Thomas Berger, Oliver Diwald

Nature and Stability of Paramagnetic Defects in Reducible Metal Oxide Nanoparticle Systems

**10.10** Markéta Zukalová, Barbora Pitřna Lásková, Ladislav Kavan  
Electrochemical Study of Na Insertion into Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>

**10.30 – 11.00** coffee break

*Chair: Martin Paidar*

**11.00** Michal Baudys, Josef Krýsa

Review of Methods for the Photocatalytic Activity Assessment of Various Building Materials

**11.20** Boštjan Žener, Romana Cerc Korošec

Nitrogen and Sulfur Doped Titania Thin Films

**11.35** Jakub Mališ, Martin Paidar, Karel Bouzek

Mobile APU System Based on the PEM Fuel Cell Stack – an Energy Balancing and Air Purification Issues

**11.50** Šárka Paušová, Martin Zlámal, José Antonio Sánchez Pérez, José Luis Casas López, Josef Krýsa

Photoelectrocatalytic Degradation of Thiabendazole Using 1-D Nanostructured TiO<sub>2</sub> Photoanodes and Solar Light

**12.10** Alexandra Němečková, Martin Zlámal, Josef Krýsa, Michael Neumann-Spallart, Štěpán Kment, Zdeněk Hubička

Bi-layer TiO<sub>2</sub>/α-Fe<sub>2</sub>O<sub>3</sub> Photoanodes for Water Splitting

**12.25** Petr Dzik, Michal Veselý, Pavel Krystyník, Michael Neumann-Spallart

Planar Photoelectrochemical Cells with Vertically Separated Electrodes: Design and Fabrication

**12.45** Michael Neumann-Spallart, Petr Dzik, Michal Veselý

Planar Photoelectrochemical Cells with Vertically Separated Electrodes: Electrochemical Aspects

**13.05** lunch

**14.00 – 18.00** individual discussions

**19.30** common dinner

**21.00** Informal discussions of teachers, young researchers and PhD students about the aspects and experiences from Czech-Austrian exchange programme

## **Friday, 2<sup>nd</sup> December**

*Chair: Karel Bouzek*

**9.00** Zdeněk Hubička, Martin Čada, Jiří Olejníček, Petra Kšířová, Štěpán Kment  
Reactive HIPIMS Magnetron Sputtering of Sulphide Thin Films

**9.20** Andreas Brüger  
Stability of WO<sub>3</sub> Thin Films

**9.40** Petra Kšířová, Michaela Brunclíková, Roman Perekrestova, Jiří Olejníček, Martin Čada, František Kovanda, Zdeněk Hubička  
Preparation of Co<sub>3</sub>O<sub>4</sub> Thin Films on Stainless Steel Sieves

**10.00** Violeta Martín-Gil, Mohd Zamidi Ahmad, Roberto Castro-Muñoz, David Dlouhý, Jan Ullsperger, Vlastimil Fíla  
Membranes for Gas Separation Applications

**10.15 – 11.00** coffee break, check out from the hotel

*Chair: Michael Neumann-Spallart*

**11.00** Vlastimil Fíla, Milan Bernauer, Zdeněk Sobalik  
Methane Aromatization on Zeolite Catalysts

**11.20** Krisztina Kocsis, Vit Kašpárek, Thomas Berger, Oliver Diwald  
From Dehydroxylated Particle Surfaces to Designed Interfaces

**11.35** Adam Giurg, M. Paidar  
Comparison of Carbon Materials for Capacitive Deionisation

**11.50** Magda Zlámalová, Pavel Janda, Hana Tarábková  
Poly(Methylene Blue) Modified Graphite Electrodes for the Electrocatalytic Oxidation of Hydrogen Sulfide

**12.05** Martin Prokop, Roman Kodým, Michal Carda, Tomáš Bystroň, Martin Paidar, Karel Bouzek  
Rotating Rod as an Alternative to Rotating Disk Electrode for High Temperature Applications

**12.20** Monika Klusáčková, Pavel Janda, Hana Tarábková  
Effect of Substrate Hydrophobicity on the Electrocatalytic Behaviour of Water Soluble Phthalocyanine Derivate

**12.35** final remarks

**13.00** lunch

**14.00** departures

# CONDUCTION BAND ENGINEERING IN TiO<sub>2</sub>: ELECTROCHEMISTRY, PHOTOCATALYSIS AND APPLICATIONS

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The electronic band structure of titania is of fundamental implication for numerous applications in electrochemistry and photocatalysis. The position of conduction band (CB) edge controls the reductive photocatalytic reactions (e.g. hydrogen evolution from water or CO<sub>2</sub> reduction), potential of dye-sensitized solar cell (DSC), recombination blocking in perovskite solar cells, etc. However, there is a considerable controversy about the position of CB in TiO<sub>2</sub> (anatase, rutile, including the crystals with distinguished facets). [1] Long-time debate concerns the fact that the CB edge of rutile (in contrast to anatase) is not sufficiently upshifted compared to the energy equivalent to the H<sup>+</sup>/H<sub>2</sub> reduction potential. [2] A standard electrochemical tool monitoring the CB edge is the flatband potential. It is measured by Mott-Schottky plots from electrochemical impedance spectroscopy, onset of anodic photocurrent of water oxidation or dark H<sup>+</sup> reduction, cyclic voltammetric mapping of DOS including the electron trap states, spectroelectrochemical determination of optical absorbance of CB electrons, etc. The staggered alignment in mixed phases, such as in anatase/rutile, is assumed to enhance photocatalytic activity of titania, but it is widely disputed whether the conduction band edge of rutile or that of anatase is higher. Photoelectron spectroscopy (PES) and most DFT simulations support the former, but the flatband potential measurements provide just opposite results. The controversy can be explained by taking into account the adsorption of OH<sup>-</sup> and H<sup>+</sup> ions from the electrolyte solution on the electrode surface. [3, 4] Furthermore, PES indicates that the CB edge of (001)-anatase is upshifted by 0.1 eV referenced to (101)-anatase in agreement with the DFT calculation [5] and with the electrochemical flatband potentials [6] (upshift of CB by 60 meV) but there are again some conflicting works claiming the opposite (see Ref. [7] for discussion).

## Acknowledgement

This work was supported and by the Czech Ministry of Education, Youth and Sports (contract No. 8F15003) and by the Czech National Science Foundation (contract No. 13-07724S).

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## STABILITY AND STRUCTURE OF TiO<sub>2</sub> SURFACES IN LIQUID WATER

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Titanium dioxide (TiO<sub>2</sub>) offer wide range of properties that can be utilized in many industrial applications such as photocatalysis, dye-sensitized solar cells, etc. At present the surfaces are well understood under UHV conditions, however in most of industry-relevant applications the surfaces are immersed in liquid. Understanding the processes closer to real application conditions at atomic scale is crucial for further improvement and better efficiency.

Therefore a combined study was carried out where well-prepared and well-characterized surfaces in UHV were exposed to liquid water and consequently analyzed with UHV techniques (STM, XPS, LEIS, LEED) again. To do that we used a dedicated system that allows controlled and clean transfer of the studied sample between UHV chamber and electrochemical cell.

The two lowest energy termination of TiO<sub>2</sub> Rutile, the (110) and (011) surfaces were studied. The results show that (110) bulk-truncated (1x1) surface is retained upon contact with liquid water with an additional twofold symmetry along the fivefold coordinated Ti rows originating probably from atmospheric contamination [1]. The results are also in agreement with in-situ STM studies performed, where atomically resolved STM images in liquid H<sub>2</sub>O and also in HClO<sub>4</sub> electrolyte show UHV-like (1x1) surface structure.

The second most common facet of TiO<sub>2</sub> Rutile, the (011) surface exhibits (2x1) reconstruction in UHV. Based on DFT predictions the (2x1) reconstructed surface is no longer favorable in liquid water environment [2]. The experiments carried out indicate change in surface structure upon contact with liquid water. However the possibility of contaminant-induced restructuring and unintentional mixed oxide formation [3,4] had to be carefully excluded.

### References

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- [4] Halpegamage *et al.*, JPCP 120 (2016), 14782-14794.

# A NOVEL APPROACH IN SOLID OXIDE PHOTO-ELECTROCHEMISTRY: BASIS FOR THERMALLY ACTIVATED SOLAR ENERGY CONVERSION

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Photon driven electrochemical reactions may contribute to future sustainable energy supply. Many different oxides (e.g. TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub>) have been tested so far to achieve photo-(electro-)chemical water splitting. Nevertheless, efficiency and/or materials stability are still not sufficient for widespread application of systems based on aqueous electrolytes. Photo-electrochemistry using solid oxide electrolytes, on the other hand, is an almost unexplored field. In such cells, operation temperatures of several hundred °C are required to enable sufficient oxide ion conduction. Very little knowledge is available on the experimental realization of such cells and on their problems.

Here, we report results on the realization of a *Solid Oxide Photo-Electrochemical Cell* (SOPEC) using oxide ion conductors, operating at 400-500°C. The SOPEC includes a high temperature photovoltaic cell based on SrTiO<sub>3</sub> in contact with La<sub>0.8</sub>Sr<sub>0.2</sub>CrO<sub>3</sub>, and a solid oxide electrolyte (Y doped zirconia). The photovoltaic cell part leads to open circuit voltages up to 920 mV at 400°C. The UV induced driving force is used in the electrochemical part of the cell to pump oxygen from low to high partial pressures, i.e. to convert radiation energy to chemical energy. This demonstrates the feasibility of high temperature photo-electrochemical cells for solar energy storage. The detailed characterization of the different resistance contributions in the system by DC and AC methods reveals the parts of the cell to be optimized for finally achieving high temperature photo-electrochemical water splitting.

## References

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# ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL PROPERTIES OF TANTALUM DOPED TITANIA THIN FILMS

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Dye-sensitized solar cells (DSCs) and solid state dye-sensitized solar cells (SSDSC) present an attractive alternative to solid state photovoltaics at competitive cost. The generic concept of DSC is a liquid-junction photoelectrochemical cell with a dye sensitized nanocrystalline TiO<sub>2</sub> photoanode. It contacts electrolyte solution with redox mediator, which transports hole from the photooxidized dye towards the counterelectrode. In solid-state dye sensitized solar cell are the photogenerated holes transported by a solid conductive material (spiro-OMeTAD)<sup>1</sup>.

The electrodes of DSSCs are often fabricated from conducting transparent oxides (TCO), such as fluorine doped tin oxide SnO<sub>2</sub>:F (FTO) or indium-tin oxide (ITO) serving as current collectors<sup>2</sup>. The TCOs are used for fabrication of both photoanode and the counter electrode (cathode), and contribute considerably to the cost of DSSCs.

Alternative material as a replacement for TCO coating is Ta-doped titanium dioxide. To obtain highly conductive polycrystalline TiO<sub>2</sub>-based TCOs, it is necessary to use a two step approach, which involves deposition of amorphous film followed by thermal treatment in reducing atmosphere (vacuum). For such doped samples it is possible to achieve low resistivity (of the order  $5 \times 10^{-4} \Omega\text{cm}$ )<sup>3</sup>.

The aim of this work was the electrochemical and photoelectrochemical characterization of thin transparent Ta-doped titanium dioxide films prepared by pulsed laser deposition. The quality of layers was tested electrochemically by cyclic voltammetry with K<sub>4</sub>[Fe(CN)]<sub>6</sub> / K<sub>3</sub>[Fe(CN)]<sub>6</sub>, dimethylviologen (MV<sup>2+</sup>) and Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as model the redox probes. Mott-Shottky analysis was used to obtain flat band potential and donor density, photoelectrochemistry for the evaluation of photocurrent response.

## Acknowledgement

This work was supported by the Grant Agency of the Czech Republic (contract No. 13-07724S).

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# EPR SPECTROSCOPY FOR THE ANALYSIS OF PARAMAGNETIC SPECIES IN THE TITANIA-BASED PHOTOCATALYTIC SYSTEMS

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The growing activity in the field of photocatalytic systems applied for the purification and remediation of polluted environments has initiated an intense research of semiconducting materials used as photocatalysts. Among them titanium dioxide still attracts substantial attention, due to the specific properties of titanium dioxide polymorphs and their ability to produce electron – hole pairs upon UV photoexcitation. The successful practical application of photocatalytic processes under real conditions requires further enhancement in the photocatalytic efficiency and the increase of visible-light activity of titania-based photocatalysts. Consequently, the detailed examination and understanding of the primary steps in photocatalytic reactions are essential for the development of photocatalysts with the desired properties [1].

EPR spectroscopy represents an important technique in the study of titania photocatalysts, providing valuable information on the paramagnetic point defects caused by high-temperature treatment during TiO<sub>2</sub> synthesis, as well as on the paramagnetic centers produced *via* the trapped photogenerated electrons and holes [2]. The photoelectrons are attributed to the surface or bulk Ti(III) ions characterized with the broad or narrow specific EPR signals with the *g*-values below 2.0 [3]. Under air, the photoelectrons or surface Ti(III) species may react with the adsorbed molecular oxygen producing superoxide radical anion, and the recent investigations pointed to rutile as a particularly good photocatalyst for the activation of molecular oxygen [4]. The photoinduced holes are recognized as the O<sup>-</sup> species characterized with a variety of signals (*g*-values > 2.0) reflecting sensitively the character of TiO<sub>2</sub> crystal lattice, as well as localization of paramagnetic species in the core of nanoparticles or on the surface [3]. The photoexcitation of oxygenated particulate TiO<sub>2</sub> systems is coupled with the generation of non-persistent radical species, and *in situ* EPR spin trapping technique is a suitable method for the indirect detection of reactive oxygen species [5].

Our contribution illustrates the potential of EPR spectroscopy in the characterization of paramagnetic species present in TiO<sub>2</sub> matrix before exposure, as well as those generated upon *in situ* photoexcitation of TiO<sub>2</sub> nanopowders. The merits and limitations of the EPR spin trapping technique in the identification of reactive radical intermediates generated upon photoexcitation in TiO<sub>2</sub> particulate systems are discussed and supported by a large number of EPR investigations.

## **Acknowledgements**

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## ATOMIC SCALE STUDIES OF THE HEMATITE (012) SURFACE

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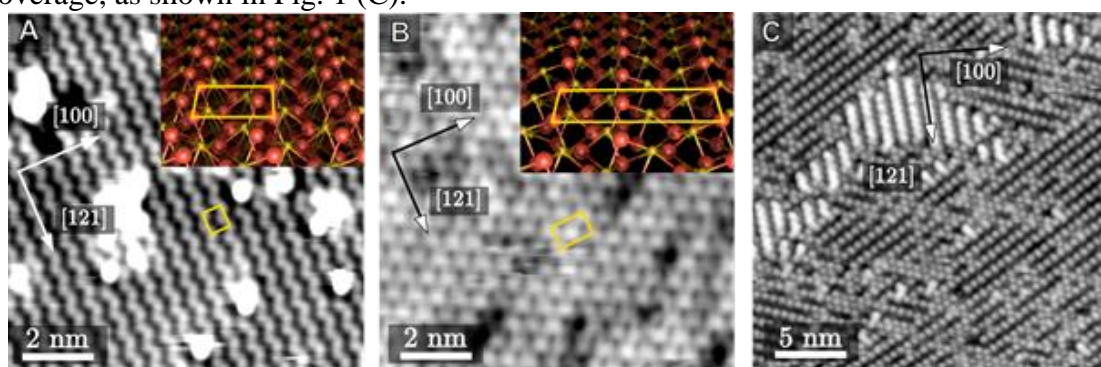
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Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is a promising material for technological applications due to its abundance, low cost and chemical stability. Its 2 eV bandgap makes it potentially ideal as a photoanode for photoelectrochemical water splitting [1], but performance is hampered by slow reaction kinetics and the need for a significant overpotential. Surprisingly little is known about the atomic scale structure of hematite surfaces in ultra-high vacuum, and even less in the aqueous environment.

To date, most surface science studies have focussed on the (001) surface, but preparing a reproducible surface has proven problematic. A few studies [2][4] have investigated the equally relevant (012) surface, and reported that a (1x1) and (2x1) termination can be reversibly prepared by varying the preparation conditions.

Here we present an atomic-scale scanning tunneling microscopy (STM) study of the (1x1) and (2x1) surfaces of  $\alpha\text{-Fe}_2\text{O}_3$ . The data acquired for the (1x1) termination support a bulk termination model, as shown in Fig. 1 (A). Images of the (2x1) reconstruction, such as that shown in Fig. 1 (B), are clearly inconsistent with a simple missing row structure [2], and we propose a model based on ordered oxygen vacancies. The plausibility of this model is confirmed by preliminary density functional theory (DFT) results.

The adsorption of water was studied on both terminations using x-ray photoelectron spectroscopy (XPS) and STM. The acquired XPS results show that all water adsorbed at room temperature is dissociated, in agreement with previously published TPD results [3]. STM images of water on the (2x1) reconstruction show two distinct ordered phases, depending on  $\text{H}_2\text{O}$  coverage, as shown in Fig. 1 (C).



**Figure 1:** STM images of the hematite (012) (1x1) termination ( $U = -3$  V,  $I = 0.1$  nA) (A), the (2x1) reconstruction ( $U = -1$  V,  $I = 0.1$  nA) (B), and of dissociated water on the (2x1) reconstructed surface ( $U = -2$  V,  $I = 0.1$  nA) (C). The insets to (A) and (B) show the bulk terminated surface and the proposed reconstruction. The (1x1) and (2x1) unit cells are marked in yellow.

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# PREPARATION AND PHOTOELECTROCHEMICAL PROPERTIES OF MIXED HEMATITE-TITANIUM DIOXIDE TRANSPARENT NANOTUBULAR LAYERS

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With increasing demands on usage of clean and sustainable sources of energy, solar water splitting seems to be promising method of preparation of energy carrier – hydrogen. To use this method, the choice of an appropriate photoanode is essential. Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is a promising photoanode candidate for photoelectrochemical water splitting due to its appropriate optical band gap (2.1 eV), its stability in many different electrolytes and low cost. However, the use of hematite is limited by short diffusion length, low conductivity and low charge separation, which is a consequence of short excited state lifetime. Moreover, the conduction band of hematite is too low to reduce water. To enable the solar water dissociation, a DC bias has to be applied. Another widely used candidate for water splitting is titanium dioxide ( $\text{TiO}_2$ ) with unique optical and electrochemical properties and chemical stability. However,  $\text{TiO}_2$  is photoactive only under the UV irradiation, because it has a large band gap energy (3-3.2 eV). The photoanode based on a mixture of  $\text{TiO}_2$  and hematite can enhance the efficiency of solar water splitting [1].

Transparent electrodes have advantage in photoelectrochemical systems where irradiation of both electrodes is necessary such as tandem solar cells. Transparent conductive oxide (TCO) substrate as fluorine doped tin oxide (FTO) layered glass provide possibility to back side irradiation of the layer and potential increase of its photoresponse.

This work describes the anodic preparation of transparent mixed  $\alpha\text{-Fe}_2\text{O}_3\text{-TiO}_2$  nanostructured photoanodes from Fe-Ti metallic films deposited by high-power impulse magnetron sputtering (HiPIMS) on the transparent conduction substrate [2]. Samples with different Fe/Ti ratio were prepared in one deposition cycle, depending on the position relative to the Fe and Ti target in the plasma chamber. Prepared Fe-Ti layers were electrochemically oxidized by applying a DC voltage in the electrolyte containing  $\text{NH}_4\text{F}$  and water in ethylene glycol. Anodization time depended on the thickness of the layer and composition of the alloy. The end of anodization was detected optically, when prepared layer became transparent. Samples were annealed in air at 500 °C.

Prepared transparent layers have nanotubular structure with thickness up to 1400 nm with expansion factor 2.5. Its photoelectrochemical properties show that increasing amount of titanium up to 13 wt% results in 6-fold higher photocurrent compared with the layer prepared from pure iron by the same technique.

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## KEY PARAMETERS FOR CONTROLLED SPACING OF ANODIC TiO<sub>2</sub> NANOTUBES

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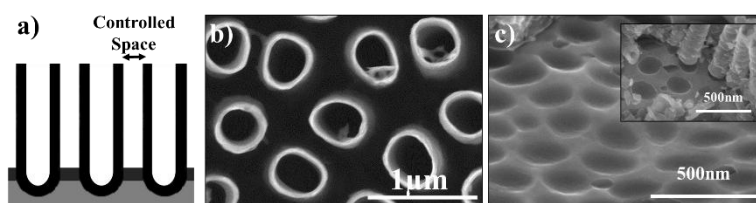
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Since the first reports on self-ordered nanotube or nanopore growth on Ti or Ti alloys by electrochemical anodization by Assefpour-Dezfuly [1] and later by Zwilling et al. [2], Gong et al. [3] and Beranek et al. [4], TiO<sub>2</sub> nanotubes (NTs) have been explored for a wide range of applications and have become one of the most investigated nanostructures over the past decade. Meanwhile, a wide range of morphological variations has been accomplished and explained such as bamboo tubes, branched tubes, or single walled TiO<sub>2</sub> NTs [5]. Moreover, tube layers that provide truly spaced regular arrays of individual tubes and control over this intertube distance could be attained [6].

Well separated spaced NTs are expected to have a high potential for hierarchical structures combining high self-order and when the goal is the defined loading of a secondary material, such structures could beneficially be used for e.g. photoelectrochemical, bio applications, dye-sensitized solar cells or other energy storage applications [7].



**Figure:** a) 2-D drawing, SEM images showing b) top and c) bottom imprints of spaced NTs.

In the present work, we show how to grow and control self-organized TiO<sub>2</sub> nanotube arrays that have defined and regular gaps between individual nanotubes. We identify critical parameters that define the “region of existence” i.e. under which condition tube spacing occurs as well as the intertube distance.

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# PHTOCATALYTIC H<sub>2</sub> GENERATION USING DEWETTED NOBLE METAL DECORATED TiO<sub>2</sub> NANOTUBES: OPTIMIZED DEWETTING AND OXIDE CRYSTALLIZATION BY A MULTIPLE ANNEALING PROCESS

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In present work, we discuss an approach to produce highly defined noble metal nanoparticle arrays where nanoparticles are placed on a TiO<sub>2</sub> nanotube stump. Key is to deposit thin metal layers on the NT surface of the nanotubes and to transform into Au nanoparticles by thermal dewetting. For perfect metal particles-ordering extremely well ordered TiO<sub>2</sub> NT layers are required. These are produced by anodizing Ti foils in a hot mixture of HF and H<sub>3</sub>PO<sub>4</sub>.

We investigate these Me@TiO<sub>2</sub>-NT substrates for the photocatalytic production of H<sub>2</sub> from ethanol. Dependent on the metal particles loading, and the annealing condition highly optimized catalyst geometries can be formed. These Me@TiO<sub>2</sub> NT exhibited a H<sub>2</sub> production rate ca. 13 or 20 times higher than that of Me NPs-decorated compact TiO<sub>2</sub> films. These results show that the geometrical features of our new photocatalytic platform can largely enhance the H<sub>2</sub> production ability of photocatalytic systems.

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# COLLOIDAL NANOPARTICLE PROCESSING AND WATER SPLITTING CATALYST PREPARATION

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In this work, we explored the impact of different colloidal parameters that may influence the activity of a nanostructured and composite metal oxide photocatalyst. The first part of this study is about surface charge adjustment of titanium oxide (anatase) and zinc oxide (wurtzite) nanoparticles in aqueous dispersions. Opposite charging of these two oxide particles types originating from metal organic chemical vapor synthesis (MO-CVS) was used to introduce heterojunctions between particles of the two and dissimilar oxides [1,2]. We prepared heteroagglomerates from TiO<sub>2</sub> and ZnO suspensions with different mixing ratios and employed the addition of Zinc citrate for surface charge adjustment. The presence of heterojunctions is expected to enhance the photocatalyst's activity in the water splitting reaction [1,3]. To explore this potential effect on samples, the colloidal properties of which were monitored at different stages of photocatalyst production, we also addressed the question whether the photocatalyst's surface is subject to changes during the photodeposition of platinum clusters as co-catalyst [4]. Associated optical property changes were measured by UV/Vis and photoluminescence spectroscopy and related to relevant developments in surface charge and particle-size distribution as determined from dynamic light scattering measurements. Finally, we measured the differential photocatalytic activity of Pt decorated heteroagglomerate nanoparticles inside a batch quartz reactor. We observed a strong negative effect of zinc oxide on the hydrogen production yield of the heteroagglomerates and will discuss its origin in the light of ZnO photocorrosion and active site blocking steps [5].

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## PHOTOINDUCED REACTIONS OF COMPOSITE g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> PHOTOCATALYSTS

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The photoinduced processes on titanium dioxide surface are significantly influenced by various aspects including the crystal structure of the photocatalyst, particle size, morphology and porosity of the nanoparticles, nature and density of the surface defects, band-gap energy and the position of edge of valence and conduction bands. Thus, the main approaches in the synthesis of titania with improved photoactivity focus on the modification of the electronic/optical properties and the structure of the photocatalyst by metal/non-metal doping or by the controlling of the microstructure and morphology of the synthesized nanocrystals. A wide interest is pointed to the synthesis of composite photocatalysts consisting of titania and organic metal-free and visible-light-driven components. The graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) was identified as a promising form of organic polymer-like material with the visible light (VIS) activity, however the small surface area and rapid electron-hole recombination hinder its practical applications. The combination of g-C<sub>3</sub>N<sub>4</sub> with TiO<sub>2</sub> can utilize the advantages of both materials and the overall photocatalytic activity of the material can be improved. The composite photocatalysts can be prepared by different synthetic pathways, e.g. annealing of titanium dioxide with melamine or hydrothermal/sol-gel reactions of titania precursors with melamine. The method of preparation strongly influences the morphology and structure of the composites formed, as well as their photocatalytic activity [1-3]. The EPR spectroscopy allows the direct detection and characterization of paramagnetic defects in solid titania matrix, as well as the identification of non-persistent paramagnetic intermediates *via* indirect methods, e.g. spin trapping technique [4].

Our study was focused on the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> composites prepared by the annealing of various ratios of dry melamine and TiO<sub>2</sub> P25 at 550 °C [3]. The X- and Q-band EPR spectra of the powdered composites were measured at room temperature and 100 K in dark. The X-band EPR signals of photogenerated charge carriers formed upon UVA and VIS light exposure of g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> were monitored in solid state at 100 K. The photocatalytic activity was also tested using the spin trapping technique in aqueous and dimethylsulfoxide suspensions in the presence of molecular oxygen upon UVA and VIS exposure. The results showed that paramagnetic species formed upon exposure sensitively reflect the reaction conditions and the influence of weight ratio of g-C<sub>3</sub>N<sub>4</sub> and TiO<sub>2</sub> in the photocatalysts. The better photocatalytic activity upon UVA and visible-light exposure was found for the composites with lower amount of g-C<sub>3</sub>N<sub>4</sub>.

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# PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF MODIFIED 2D-TITANIUM DIOXIDE NANOSHEETS

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Titanium dioxide and its photocatalytic applications are still the most discussed topic. However, in view of the fact that titanium dioxide nanoparticles still exhibit several limitations impeding their wide range of industrial utilization, the doping or modifying of TiO<sub>2</sub> are currently intensively studied as one of the possibilities to improve its photocatalytic properties. Aim of this work was to modify 2D-TiO<sub>2</sub> nanosheets to shift their light absorption to the visible-light region.

In the first step of the preparation of non-modified material, titanyl sulphate was dissolved in distilled water. The colourless solution was precipitated by ammonia solution until pH 8. The white precipitate was filtered and washed to remove SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> formed in the reaction. Then the pH value was reduced by adding hydrogen peroxide. The resulting yellow transparent colloidal suspension of peroxo-polytitanic acid was lyophilized, and subsequently annealed at 300, 500, 650, 800 and 950 °C [1,2,3]. The samples were modified with silver, gold or neodymium (dopant was added in the first step of synthesis in amount of 1 % at. towards Ti), and with nitrogen (dopant was added in the last step of synthesis, urea and TiO<sub>2</sub> was in the ratio of 1:10, 1:2, and 1:1).

2D-TiO<sub>2</sub> samples were studied by X-ray diffraction, electron microscopy, and the specific surface area was determined by the B.E.T. method. The photocatalytic activity was characterized using 4-chlorophenol (4-CP) in an aqueous solution as a model compound.

Lyophilization of colloid suspension leads to the formation of foils consisting of nano-sized crystalline nuclei of peroxo-polytitanic acid dispersed in predominantly amorphous material. The results of detailed morphological and phase characterization revealed that the annealing at temperatures up to 800 °C resulted in the formation of 2D-foils composed of packed anatase nanocrystals and the anatase/rutile mixture was observed at annealing temperature of 950 °C.

In comparison with unmodified sample and standard P25 (Evonik-Degussa), the modified samples did not yield an increase of the photocatalytic activity in UV region and the photocatalytic activity in visible region was even about 2 orders lower than in UV.

## Acknowledgement

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## EPR STUDY OF DOPED LAMELAR ANATASE NANOPARTICLES

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Pristine anatase photocatalysts absorb mainly the ultraviolet radiation, which rules out the utilization of the solar light as a suitable irradiation source in the TiO<sub>2</sub> based photocatalysis. Among the extensive efforts devoted to overcome this limitation and extend the spectral response to the visible light region, the doping represents one of the promising approaches to prepare suitable anatase nanomaterials. A large number of studies deal with the doping of TiO<sub>2</sub> with charged or neutral metallic or non-metal species.

EPR spectroscopy represents a suitable technique in the investigations of titania photocatalysts, especially in the research of modified titanium dioxide materials, as it allows a direct monitoring of paramagnetic centers and reactive radical intermediates providing valuable information on the trapped photogenerated electrons and holes in TiO<sub>2</sub> lattice [1]. Based on the position and character of the specific EPR signals, Ti(III) ions representing the trapped photoelectrons and the O<sup>-</sup> species assigned to the photoinduced holes can be distinguished. These species are characterized with a variety of signals reflecting the character of TiO<sub>2</sub> crystal lattice, as well as the localization of paramagnetic species in the core of nanoparticles or on the surface. Under air, the photoelectrons may react with adsorbed molecular oxygen producing superoxide radical anion (O<sub>2</sub><sup>•-</sup>) or hydroperoxy radical (•O<sub>2</sub>H), also detectable by EPR. Furthermore, the doping together with the high-temperature treatment under specific atmosphere applied during the synthesis of nanocrystalline TiO<sub>2</sub> materials can induce the formation of various defects or paramagnetic centers in the titania lattice which affect the optical and electrical properties of the material.

A series of highly UV photoactive 2D anatase nanostructures (leaflets) was prepared and characterized by Šubrt et al. [2,3], consequently, taking into account the demand for the photocatalysts active under visible light the metal and nitrogen doping was applied. The presence of paramagnetic centers in the studied nanostructures was followed by the EPR spectrometer (EMX Bruker) working in the X- or Q-band at different temperatures in the range 100–250 K [4]. The EPR spectra were recorded before, upon/after photoexcitation either using the monochromatic LED source with the wavelength of 365 nm or polychromatic visible light (KL 1600LED, T = 5600 K).

### Acknowledgement

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## NATURE AND STABILITY OF PARAMAGNETIC DEFECTS IN REDUCIBLE METAL OXIDE NANOPARTICLE SYSTEMS

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The electronic properties of semiconducting metal oxide nanoparticle systems are determined by nature and abundance of point defects. Their characterization and manipulation is challenging and requires the comprehensive discussion of the materials' environment and history. Electron paramagnetic resonance (EPR) spectroscopy is an excellent technique to investigate paramagnetic defects and, in particular, to characterize the electronic structure of electron centers in reducible metal oxide particle systems such as TiO<sub>2</sub> or ZnO. [1,2]

ZnO and TiO<sub>2</sub> nanoparticle systems were prepared by metal-organic chemical vapor synthesis and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and UV/Vis spectroscopy. Different procedures for defect generation, e.g. annealing under high vacuum conditions ( $p < 10^{-6}$  mbar) and controlled gas atmospheres (O<sub>2</sub>) were applied and the paramagnetic properties of resulting particle powders were described. Defect concentrations critically depend on the residual oxygen partial pressure. The reactivity of emerging defect electrons towards adsorbed oxygen and water was studied and information on location (in the bulk or at the surface of the particles) and energy of the defect states within the bandgap of the semiconducting material was obtained. As a result of electron transfer reactions between reactive defects present on non-stoichiometric and defective metal oxide samples and molecular oxygen, superoxide species (O<sub>2</sub><sup>-</sup>) are generated and utilized as paramagnetic surface probes. We tracked these processes with EPR and UV/Vis/NIR spectroscopy. The impact of adsorbed water on the interfacial charge transfer reaction will be discussed in detail.[2]

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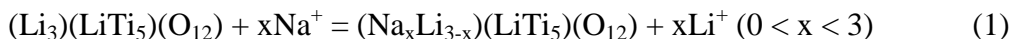
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## ELECTROCHEMICAL STUDY OF NA INSERTION INTO $\text{Li}_4\text{Ti}_5\text{O}_{12}$

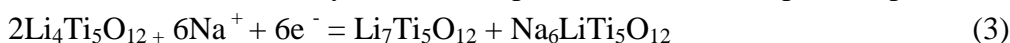
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Recently,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (spinel, LTS), used as the negative electrode material in Li-ion batteries, has also been examined for the Na-ion battery. Na insertion in  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  is accompanied with development of Na-substituted LTS phase with an about 4-5% larger unit cell volume which co-exists with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  in a single particle[3].



DFT calculations made by Sun et al[4] predicted even three-phase separation mechanism,



In our work we studied Na insertion into LTS of different particle size and synthetic history by means of cyclic voltammetry and galvanostatic chronopotentiometry. The structural changes induced by Na insertion were studied by Raman spectroscopy. The highest capacity and charging rate for Na insertion exhibited nano LTS prepared by sol-gel process pioneered in our laboratory[1, 2]. Charge capacities calculated from extraction branch of cyclic voltammogram were 156 mAh/g and 75 mAh/g for nano LTS and microcrystalline Aldrich LTS respectively. However considerable nano LTS capacity drop of about 40 % was observed during cycling. This is obviously the consequence of irreversible structural changes induced by Na accommodation in the lattice. To identify these structural changes nano LTS after several cycles of Na insertion/extraction was studied by Raman spectroscopy. Except LTS peaks the spectrum exhibited features of orthorhombic  $\text{Li}_{0.5}\text{TiO}_2$  phase, which is formed during Li insertion into anatase. There are no features of orthorhombic phase in Raman spectrum of anatase after Na insertion. Obviously, Na insertion into LTS is accompanied by partial Li redistribution into either minor anatase impurities or defects sites in LTS lattice. This process results in decrease of LTS ability to accommodate Na.

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# REVIEW OF METHODS FOR THE PHOTOCATALYTIC ACTIVITY ASSESSMENT OF VARIOUS BUILDING MATERIALS

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This contribution deals with the review of methods for the photocatalytic activity assessment of various construction and building materials. Photocatalytically active surfaces consist generally of thin films of TiO<sub>2</sub> on a suitable substrate as glass, ceramic tiles, concrete, hydraulic binders and paints. Commercial application of such surfaces is based on the three environmental functions: i) self-cleaning, ii) air cleaning and iii) antibacterial cleaning. Therefore, there is a strong need to objectively evaluate their photocatalytic function.

To assess photocatalytic activity in terms of efficiency of photocatalytic oxidation of pollutants in gas phase the four international standards (ISO 22197-1, ISO 22197-2, ISO 22197-3, ISO 22197-4) which include removal of NO<sub>x</sub>, acetaldehyde, toluene and formaldehyde are available. Methods differ, except the type of pollutant, in concentration and total flowrate. Photocatalytic activity is quantified as the amount of removed pollutant in the last hour of the test (formaldehyde, acetaldehyde, and toluene) or the amount of removed NO<sub>x</sub> during 5 hours test. The analysis of the model pollutants is accomplished by GC-FID (organic compounds) and NO/NO<sub>2</sub> chemiluminescence analyser which are relative expensive equipment to realize such kind of test (including mass flowmeters and calibration gases) [1,2].

For the quick determination of photocatalytic activity (or for demonstration/popularization purposes) it is very convenient to use more simple method based on irreversible color change of dye in ink which occurs on irradiated photocatalytic surface [3]. In contrast to so far existing ISO methods, this method is based on reduction of dye (Resazurin, 2,6-dichloroindophenol, Methylene blue) and this reduction is connected with the colour change of the dye. Due to the extent of glycerol which acts as a sacrificial electron donor the quantum yield of such reaction, in comparison to oxidative bleaching, is very high and the whole test takes few minutes. Photocatalytic activity is then expressed as a time of UV irradiation needed for the colour change of the ink film. It can be shown that the rate of ink discoloration is proportional to the rate of photocatalytic oxidation [4,5], thus this method can be used to evaluate self-cleaning ability of commercial surfaces such as paints, glass, concrete etc.

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## NITROGEN AND SULFUR DOPED TITANIA THIN FILMS

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In recent years, the area of developing highly active photocatalysts, based on titanium dioxide has been vastly investigated due to its various applications in the environment related fields. Photocatalysis is used to describe a process during which a semiconductor (titanium dioxide) interacts with light to produce reactive oxidizing species, which then react with adsorbed pollutants. The main drawback of titanium dioxide photocatalysts is that they can only be excited by UV light ( $\lambda < 380$  nm). In order to increase photocatalytic activity under visible light irradiation, materials have been doped with metals and nonmetals (nitrogen, sulfur, fluorine, carbon, phosphorus etc.).<sup>1,2</sup>

Thin films and corresponding powders were prepared by a particulate sol-gel route, using titanium tetrachloride ( $\text{TiCl}_4$ ) as a precursor. During the synthesis, different quantities of various acids (hydrochloric, sulfuric and nitric acid) were added. The latter two acids can also act as sources of sulfur and nitrogen. After the first step of the synthesis, different chemicals, which acted as sources of nonmetal dopants (urea, thiourea and ammonium nitrate) and hydroxypropyl cellulose (HPC, organic polymer, which increases the thickness and the porosity of materials) were added. These sols were then deposited onto object glasses by dip-coating technique and then thermally treated in a muffle furnace at different temperatures to enhance crystallization of titanium dioxide.

Thermogravimetric analysis (TG) and X-ray powder diffraction (XRD) were used to determine the temperature of thermal treatment. XRD was also used to determine the crystal modification and to estimate crystallite sizes of titanium dioxide. Scanning electron microscopy (SEM) images were used to investigate the surface of our materials. Photocatalytic efficiency of the thin films was determined by measuring the degradation rate of Plasmocorinth B (PB), an organic pigment, which belongs to the group of azo dyes. Azo dyes are used in textile industry as textile colourants. They have been shown to damage ecosystems when expelled into water systems, and pose very serious health risks to humans, because they can form aromatic amines, which are potentially carcinogenic substances.<sup>3</sup> Results have shown that the photocatalytic efficiency of the thin films depends on temperature of thermal treatment, type of acid used, the type of dopant and its molar concentration.

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# MOBILE APU SYSTEM BASED ON THE PEM FUEL CELL STACK - AN ENERGY BALANCING AND AIR PURIFICATION ISSUES

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Portable power sources and/or auxiliary power units (APU) represent nowadays and important field of development. It is connected with rapid wide spreading of different control, communication and other electronic systems becoming crucial for many domains of human live. PEM type fuel cells represent promising approach to accomplish this task having important advantages when compared to the conventional batteries or to the combustion engine based technologies. They are characterized by efficient conversion of chemical energy carried by fuel into electrical energy and by a silent operation. Beside electricity main products of PEM fuel cells operation are pure water and heat. These facts represent main reasons, why the fuel cell stacks can be successfully used as portable power sources e.g. for mobile medical beds or in field hospitals, rescues operations in outlying areas, or backup power source for firefighters and police. Mobile PEM fuel cell based APUs can also be used as a backup power source for telecommunication transmitters or meteorological stations. In all these applications weight represents a very important factor. It cannot overstep the upper limit of 15 kg. Air is typically used as an oxidant to reduce weight and size of the system, as the oxygen gas cylinder is in such a case avoidable.

Using of an ambient air as an oxidant is potentially dangerous from the fuel cell lifetime point of view. Atmospheric air contains typically solid impurities, like dust and pollen, which can deposit on cathode surface and block the gas distribution channels and/or gas diffusion layer. Therefore it is necessary to use precise multi-degree filtration with level for trap of all particles larger than 1  $\mu\text{m}$ . Also platinum nanoparticles used as a catalyst are easily poisoned by the various pollutants often presented in the air, especially in the industrial agglomerations, or in the area of accidents. Most dangerous are hydrogen sulfide and other volatile sulfur containing compounds. These are known to be strong poisons for platinum catalyst, with impossible regeneration. The second group of potentially dangerous pollutants are organic compounds, e.g. benzene and toluene, which can adsorb on and block the catalyst surface. In order to minimise the danger of catalyst poisoning, the active carbon filter is typically incorporated to the system to purify air supplied to the fuel cell.

Regarding the stack operation strategy from the point of view of its size and efficiency, satisfactory compromise has to be found. PEM fuel cells reach highest efficiency at a low load, which, however, leads to oversized units for desired production capacity. At the same time, dynamic energy load has to be taken into the account when designing mobile backup power unit. To avoid utilization of an oversized PEM stack, suitable energy balancing system is required. It is typically realized by the correspondingly sized batteries or supercapacitors. Some types of batteries, e.g. NiCd, are sensitive to low temperatures, another, e.g. lithium ion, to the overheating of battery pack. Supercapacitors possess significant advantages, like high energy density instantly accessible for consumption and no-memory effect. On the other side, batteries are characterised by much better energy/weight ratio than supercapacitors.

From the above follows, that for designing auxiliary mobile power supply, a number of issues has to be considered. The issues discussed above, i.e. air supply subsystem and energy balancing of the APU unit, are the topics of the present contribution.

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# PHOTOELECTROCATALYTIC DEGRADATION OF THIABENDAZOLE USING 1-D NANOSTRUCTURED TiO<sub>2</sub> PHOTOANODES AND SOLAR LIGHT

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With increasing demands on removal of harmful and persistent organic compounds, which are often non-biodegradable, the effort is given to the development of efficient methods for their removal. One of these methods is photocatalytic oxidation which belongs to the large group of so called Advanced Oxidation Processes (AOP). Photocatalytic oxidation of organic pollutants can be improved by an application of external bias which results in an efficient separation of photogenerated charges. This process, in which the photocatalyst film (e. g. TiO<sub>2</sub>) on a suitable support serves as photoanode, is an extension of the photocatalytic process.

Although, TiO<sub>2</sub> is a suitable candidate for photoelectrocatalytic degradation of pollutants, some main drawbacks have to be overcome (high electron-hole recombination or short excited state life time). Furthermore, due to the rather high band gap energy (3.2 eV) TiO<sub>2</sub> can absorb only UV light (up to 400 nm) which represents approximately 3% of the solar spectrum. One of the strategies how to improve the photoelectrocatalytic degradation rate is the preparation of 1-D nanostructured TiO<sub>2</sub> photoanodes which can improve the speed of photogenerated electrons to the back contact of the photoanode. The other issue is the utilization of solar light which can be used either directly [1], or through the application of UV LEDs supplied by the electricity from solar PV panels.

The aim of the present work was thus the experimental evaluation of usage of 1-D TiO<sub>2</sub> photoanode for the photoelectrochemical removal of a model water micropollutant Thiabendazole (TBZ) from water using solar light. TBZ is a potent anthelmintic and fungicide used in the treatment of parasitic infections in humans and domestic animals and post-harvest protection of agricultural commodities [2]. TBZ may have carcinogenic effects at high concentrations [3].

The TiO<sub>2</sub> 1-D nanostructures were prepared by anodization of various Ti substrates [4]. The photoreactor applicable for photoelectrocatalytic degradation of organic compounds in liquid phase was designed and connected with two different light sources: concentrated (10-50 W m<sup>-2</sup>) solar light and low cost UVA LED light of different intensities (30 and 50 W m<sup>-2</sup>). The crucial investigated parameter was the applied bias. The applied value 0.5 V increased the value of reaction rate constant by 50 % (in relation to open circuit situation).

## Acknowledgements

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## BI-LAYER TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> PHOTOANODES FOR WATER SPLITTING

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Titania (TiO<sub>2</sub>) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) have potential applications as semiconducting photoanodes for hydrogen production via photoelectrochemical water splitting. The advantages of TiO<sub>2</sub> are its low price, high stability and nontoxicity. However, only a very small part of sunlight (4%) is absorbed. Iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has a favourable band gap (2.0–2.2 eV), which allows absorbing a substantial fraction of the solar spectrum, resulting in the theoretical maximal solar-to-hydrogen (STH) conversion efficiency of 15% [1]. But there are also limitations, e.g. the nonideal position of hematite's conduction band, which is too low for spontaneous water reduction or low stability in acidic media. The latter can be minimised by the coverage by the thin titania film. Furthermore it was recently verified that thermal treatment of such  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nano-heterostructures may lead to the formation of an ultrathin film of pseudobrookite iron titanate (Fe<sub>2</sub>TiO<sub>5</sub>) which resulted in the significant improvement of the PEC efficiency [2]. Further work then revealed that the heterojunction between the hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and pseudobrookite (Fe<sub>2</sub>TiO<sub>5</sub>) film significantly affects the charge separation process, resulting in considerable increase of long-lived valence band holes at the surface [3]. Therefore, the aim of the present work was the preparation and photoelectrochemical characterization of bilayer TiO<sub>2</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films.

All layers were prepared on conductive fluorine doped tin oxide (FTO) glass (Solaronix, TCO22-15). Bi-layers of TiO<sub>2</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were prepared by subsequent deposition of TiO<sub>2</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> layers. Nonporous TiO<sub>2</sub> layers were prepared by the sol-gel method using dip-coating [4]. Layers of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were prepared by high-power impulse magnetron sputtering (HiPIMS) described previously [5]. Deposited layers were annealed at 650 °C.

Photo-electrochemical measurements were performed in a glass cell using a three-electrode arrangement. Pt was used as counter electrode, Ag/AgCl as reference electrode and a solar simulator with an AM1.5G filter and irradiance of 1 sun (100 mW/cm<sup>2</sup>) was the light source. Amperometry at fixed potential and backside illumination at different wavelengths from 365 nm to 620 nm was used to determine the IPCE (incident photon to current conversion efficiency) spectrum. Photocurrent and, accordingly, IPCE is significantly higher for hematite films with a TiO<sub>2</sub> capping layer than for the sum of IPCE for single hematite and TiO<sub>2</sub> films which can be explained by a synergistic effect of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> heterostructure.

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# PLANAR PHOTOELECTROCHEMICAL CELLS WITH VERTICALLY SEPARATED ELECTRODES: DESIGN AND FABRICATION

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A novel outline of a planar photoelectrochemical cell consisting of a semiconductor layer topped by subsequent layers of a digitated insulator and a counter electrode is introduced. The use of vertically separated electrodes represents a major development in reducing the footprint (inactive areas) of planar electrochemical cells[1]. The insulating space between cathode and photoanode which is necessary in an interdigitated device [2] is reduced to a minimum as it is arranged vertically between the electrodes, just requiring a small extra space to safely ensure their absolute electrical separation. The cells, consisting of a nanoparticulate titania photoanode and a digitated, metallic cathode, were fabricated by a strictly additive process employing material printing as the exclusive deposition and patterning tool. Transparent conductive oxide coated glass and polyethyleneterephthalate sheets were used as substrates; nanocrystalline titania dispersion bonded by a novel organosilica binder was used for the fabrication of the photoanode[3] and gold or carbon inks for the fabrication of the digitated cathodes[4]. Due to the digitated shaping of the cathode, photoelectrochemical response was not suffering from  $iR$  drop down to low electrolyte ionic strengths. The printed cells were used for electroassisted photocatalytic degradation experiments with aqueous solutions of coumarin. Considerable acceleration of the coumarin degradation rate compared to the plain photocatalytic mode was observed.

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PLANAR PHOTOELECTROCHEMICAL CELLS WITH VERTICALLY SEPARATED  
ELECTRODES: ELECTROCHEMICAL ASPECTS

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Following the introduction of the concept for planar photoelectrochemical cells with vertically separated electrodes in the previous contribution, several important aspects affecting the performance of such type of cells need to be discussed. This concerns the photoelectrochemical response of the devices in dependence of the topological and electrode material choices and the way in which they influence photoelectrocatalytic efficiency.

## REACTIVE HIPIMS MAGNETRON SPUTTERING OF SULPHIDE THIN FILMS.

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A reactive HIPIMS magnetron sputtering system working in Ar+H<sub>2</sub>S gas mixture was investigated for a deposition of sulfide thin films. Semiconducting FeS<sub>2</sub> thin films were deposited on glass, TiO<sub>2</sub> and Pt coated silicon wafer. Fe target was used in this research in order to deposit pyrite FeS<sub>2</sub> thin films. Plasma parameters of HIPIMS reactive plasma was investigated by a RF ion flux probe, quartz crystal monitor modified for measurement of ionization fraction of sputtered particles and by emission spectroscopy. A wide range of values of mass flow rates of reactive gas H<sub>2</sub>S was used for the investigation of HIPIMS reactive process. It was found that the deposition rate of FeS<sub>2</sub> thin films is not influenced by the flow rate of H<sub>2</sub>S reactive gas into the discharge by the reactive deposition process although the target is covered by FeS<sub>x</sub> compound layer. The ionization fraction of reactively sputtered particles decreases from  $r \approx 40\%$  to  $r \approx 20\%$  as the flow rate of H<sub>2</sub>S changes from 0 sccm to 19 sccm at the gas pressure 1 Pa in the reactor chamber. If FeS<sub>2</sub> thin films were deposited at conditions with relatively high ionization fraction of reactively sputtered particles  $r \approx 30\%$  the atomic ratio in the as deposited films was Fe/S $\approx$ 1. In order to get pure pyrite stoichiometric FeS<sub>2</sub> structure the deposited film had to be annealed in sulphur vapors up to 400 °C. When high mass flow rate was used  $Q_{\text{H}_2\text{S}} \approx 20$  sccm and higher pressure was used we got pyrite structure and accurate stoichiometry of FeS<sub>2</sub> films without annealing in sulphur. Pyrite structure was identified in the deposited films also by XRD and Mossbauer spectroscopy.

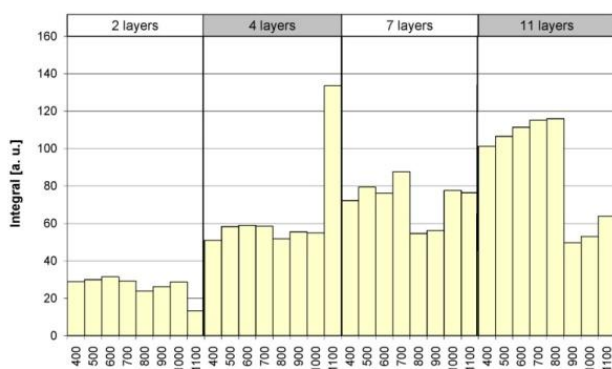
## STABILITY OF WO<sub>3</sub> THIN FILMS

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WO<sub>3</sub> is investigated as photocatalyst for its higher photoactivity under solar illumination, compared to TiO<sub>2</sub>. A major disadvantage represents the instability in solvents of different pH. Various reactions of WO<sub>3</sub> on the surface as well as in the bulk complicate a characterisation of its photocatalytic activity. Reactions to form hydrates, oxygen deficiencies or oxide bronzes are discussed.

X-diffraction analysis is well established for the structural characterisation of photocatalysts. The calcination of amorphous layers, to form stable films, is accompanied by structural changes different to the heat treatment of powders [1]. The crystallisation process can be extended over a wide temperature range, the volatilisation of solvent and the elimination of organic ligands can be inhibited.



**Figure 1:** Peak integration as the sum of the (002), (020) and (200) reflection of WO<sub>3</sub> films, as a function of the temperature, with a thickness ranging from 200 nm (2 layers) to 1150 nm (11 layers).

The incremental heating of WO<sub>3</sub> amorphous films shows a gradual increase of the crystalline phase as well as a partial loss at higher temperature (Fig. 1), up to a complete disappearance of the films.

Delamination, and phasetransfers are discussed using high resolution X-ray diffraction with in-situ annealing of WO<sub>3</sub>-films, prepared from metallo-organic precursors.

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## PREPARATION OF $\text{Co}_3\text{O}_4$ THIN FILMS ON STAINLESS STEEL SIEVES

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Recently  $\text{Co}_3\text{O}_4$  semiconductor thin films and nanostructures are of great interest for various applications as gas sensors and also for many optoelectronic and photonic applications.  $\text{Co}_3\text{O}_4$  is usually p-type semiconductor with the spinel crystalline structure and band gap in a suitable range. Cobalt oxides, namely the  $\text{Co}_3\text{O}_4$ , also show high catalytic activity in various oxidation reactions. This work is focused on comparison of two different  $\text{Co}_3\text{O}_4$  preparation techniques (i) the direct oxidation in the deposition process (RF magnetron sputtering and high-power impulse magnetron sputtering (HiPIMS)), and (ii) the thermal separation process of the deposited Co films. The possibility of utilizing the obtained  $\text{Co}_3\text{O}_4$  layer as an interlayer for adhesion improvement of electrodeposited  $\text{Co}_3\text{O}_4$  layer on stainless steel sieves was also examined.

The stainless-steel sieve (71% Fe, 16% Cr, 11% Ni, 2% Mo) with a mesh size of 400  $\mu\text{m}$  was used as a support. An RF magnetron sputtering system with SmCo magnets and 50 mm pure cobalt target was used for the deposition of metallic cobalt films with a good adhesion. These metallic cobalt films were annealed in furnace at temperature of 500 °C for 4 hours in air, resulting in a  $\text{Co}_3\text{O}_4$  films development. The further approach of the deposition was the 30 minutes of reactive magnetron sputtering (power of 200W) of metallic cobalt target in gas mixture of Ar+O<sub>2</sub>. When preparing the  $\text{Co}_3\text{O}_4$  layers using the HiPIMS technique the excitation times were set as follows: period time  $T = 15$  ms, "ON" time  $T_{\text{ON}} = 100$   $\mu\text{s}$ . The deposition time was set to 60 min. In both cases the stainless-steel sieves were covered on both sides.

The electrochemical deposition of  $\text{Co}_3\text{O}_4$  was prepared by thermal decomposition of cobalt hydroxide precursor obtained by electrochemical synthesis on the stainless-steel sieves, covered with  $\text{Co}_3\text{O}_4$  prepared by a plasma sputtering. The electrochemical deposition of precursor was performed in aqueous solution of cobalt nitrate in the presence of  $\text{KNO}_3$  as supporting electrolyte. The potentiostatic mode in a single compartment, three-electrode cell was applied; the stainless-steel sieve was used as the working electrode, the Pt foil was used as counter electrode and the potential was measured with respect to an aqueous saturated calomel electrode (SCE). The  $\text{Co}(\text{NO}_3)_2$  concentration was 0.10 mol/l,  $\text{KNO}_3$  concentration was 0.25 mol/l, potential  $-1.15$  V vs. SCE, temperature 30°C, and deposition time 1200 s. The washed sample was dried at 60°C and calcined at 500°C for 4 h in air to obtain the supported oxide catalyst.

The surface morphology and thickness of deposited  $\text{Co}_3\text{O}_4$  layers were examined by scanning electron microscope (SEM, TESCAN FERA 3) and surface profilometry (Alpha Step 500), respectively. XRD (Seifert XRD 3000 P diffractometer with  $\text{CoK}\alpha$  radiation) and Raman spectroscopy detected the crystallography of prepared layers.

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## MEMBRANES FOR GAS SEPARATION APPLICATIONS

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Membrane technologies for gas separation represent a promising technologies for different gas separations such us: upgrading of natural gas, hydrogen recovery, CO<sub>2</sub> sequestration, nitrogen enrichment, etc. In all these application, membrane technology has an important role due to the lower investment cost, easy operation, small footprint etc.

However, polymeric membranes show some limitations in order to extend their uses such as: Robenson trade-off which established permeability and selectivity have opposite behaviors, CO<sub>2</sub>-induced plasticization and aging. Different strategies have been followed in order to overcome these problems such as: synthesis of new polymers, crosslinking of the polymers, incorporation of nanoparticles to improve the gas separation performances, formation of three components membranes etc.

This contribution is reviewing our activities in the field of membrane synthesis and characterization. The membranes with potential in membrane gas separation application are discussed. In our studies, we have been focused on the synthesis of new polyimides for CO<sub>2</sub>/CH<sub>4</sub> separation, and post-treatment procedures for crosslinking membranes to avoid CO<sub>2</sub> induced plasticization such as thermal and chemical crosslinking, fabrication of Mixed Matrix Membranes (MMMs) for natural gas separation using inorganic nanostructured materials (zeolites, zeolitic imidazole frameworks, and graphene oxide) as well as ternary MMMs using polyethylene glycol as the third component in order to improve the gas separation performance of the unfilled polymer. The results of aging studies carried out under industrial working conditions in order to evaluate the potential lifetime of the membranes manufactured using the newly synthesized polyimides are discussed too. The future and perspectives based on our findings are summarized finally.

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## METHANE AROMATIZATION ON ZEOLITE CATALYSTS

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Methane dehydro-aromatization (MDA) over transitional metal doped zeolites (i.e. ZSM-5) is a non-oxidative process of methane transformation to higher hydrocarbons. This process has a potential to be an alternative to other technologies for natural gas transformation, such as methane oxidative coupling, steam reforming or methane partial oxidation. Despite of systematic study of the effects of the catalyst composition, preparation procedure, pre-treatment, and the reaction conditions was systematically followed, since the pioneering works of the Chinese group from 1993 [1], the suppression of fast deactivation of catalyst by coke deposition was still not solved successfully.

Due to the relatively fast deactivation of the catalyst by coking at reaction conditions (700 °C, 101 kPa), multiple approaches are investigated in order to stabilize the methane conversion and selectivity to benzene: (i) zeolite framework type or its modification, (ii) addition of co-catalyst, (iii) modification of the reaction conditions by addition of co-reactant or by increasing reaction pressure.

The alternative of the approaches mentioned above could be a development of stable catalyst enabling its fast and effective cyclic regeneration by oxidative procedure. The critical issues, have to be solved in this approach, are the stabilization of active metal at regeneration conditions and optimization of production and regeneration steps.

The present contribution is summarizing activities and results of our group in this field during last decade. The effects of framework type (ZSM-5, MCM-22, TNU-9), addition of second metal (Co,Ce) and order of impregnation (Co, Mo, MoCo, CoMo), distribution of alumina in frameworks of ZSM-5, working conditions (temperature, pressure, addition of co-reactant like H<sub>2</sub>, CO<sub>2</sub>) and optimization of production and regeneration steps are discussed.

Experimental results are presented in terms of concentration profiles of C<sub>2</sub>, C<sub>3</sub> and C<sub>6</sub>H<sub>6</sub> products as a function of time on stream, accompanied by the analysis of C/H ratio on the coke residua accumulated on spent catalyst.

### Acknowledgments

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## FROM DEHYDROXYLATED PARTICLE SURFACES TO DESIGNED INTERFACES

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ZnO nanostructures are extensively used in electronic devices. In this regard, materials optimization towards more efficient devices requires a comprehensive understanding of the materials' electronic properties and their dependence on sample preparation and processing.

In this study, the electronic properties of vapor phase grown ZnO nanoparticles were investigated in vacuum, in O<sub>2</sub> atmosphere and within aqueous dispersions. [1] The electronic materials' properties were modified by the generation of point defects such as excess electrons (i) via thermal annealing of particle powders at high vacuum (T = 673 K) or (ii) via accumulation of photogenerated electrons in colloidal nanoparticles (UV exposure in the presence of methanol). [2] The optical properties of the samples were investigated by UV/Vis and photoluminescence spectroscopy. [2,3]

Colloidal ZnO dispersions can be prepared via controlled replacement of the surrounding gas phase by a liquid. On these systems we have found that colloidal particle properties (hydrodynamic diameter, zeta potential) as well as the photoluminescence emission properties do not show a dependence on stoichiometry changes induced by vacuum annealing (i.e. the generation of excess electrons within the oxide lattice). The absence of these expected effects is attributed to the low concentration of excess electrons which - as a result of robust defect generation protocols - can be adjusted at the order of the number of particles. In contrast to that, we have found significant changes in both the zeta potential and the emission properties for particle dispersions exposed to UV excitation in the presence of a hole acceptor. In addition to charge accumulation, other processes such as photocorrosion need to be included in the discussion of related effects. [4] Finally, we have investigated the impact of adsorbed organic anions (acetate and citrate ions) both on the particles' surface charge and on the photoluminescence emission properties. The here investigated functional dependences provide important means for the knowledge-based design of interface determined functional materials properties of ZnO nanoparticle based materials.

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## COMPARISON OF CARBON MATERIALS FOR CAPACITIVE DEIONISATION

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Water treatment is a very important process. The large amount of water has to be treated worldwide. The most ordinary methods are distillation, reverse osmosis and electrodialysis at present time. Another promising process is capacitive deionisation (CDI) intensively studied in recent years. CDI is a very simple process for salinity reduction of treated water. The key components of CDI are high surface electrodes. Electrodes are usually from carbon material. Electrodes have to exhibit high specific surface area and pore structure suitable for ions capturing. The present work is focused to the comparison of different carbon electrodes.

Selected commercial and in-house made electrodes were examined in the simple bath cell by cyclic voltammetry and potential pulse chronoamperometry. Potential range  $\pm 1.2$  V was used for maximum ions captured on surface of electrode and to avoid undesired Faradaic reactions. Two selected electrodes were measured in the plug flow cell by potential pulse chronoamperometry. The solution conductivity at the cell output was measured in time. The conductivity was recalculated to the concentration.

The commercial material Kynol<sup>®</sup> has shown high capacity at low potential sweep velocity. But, it was showed low capacity at high potential sweep velocity i.e. limitation by transport of ions was there. The explanation is relatively high thickness of electrode 0.5 mm and high number of micro pores. The high capacity of this electrode can be utilized if time for ion transport to the electrode will be sufficient during CDI operation regime. It was confirmed in the plug flow cell. Almost constant response was found for carbon cloth with deposited microporous layer (Am) i.e. there was no limitation of ions transport but the capacity was very low. The in-house made electrode (V8) has had similar properties like the Kynol<sup>®</sup> but the observed capacity was a bit lower. Another in-house electrode (KS) has had similar capacity like Kynol<sup>®</sup> at high potential sweep velocity but it has had significantly higher capacity than Kynol<sup>®</sup> at low potential sweep velocity i.e. that this electrode has pores more suitable for ions capturing than Kynol<sup>®</sup>. Capacities of the selected electrode materials are summarized in the table below.

**Table 1:** Stored charge of CDI electrodes, measured in interval -1.2–1.2 V in 1 mol/dm<sup>3</sup> KCl.

Electrode	Stored charge in mC/cm <sup>2</sup> at different potential sweep velocity		
	100 mV/s	10 mV/s	2 mV/s
Kynol <sup>®</sup>	10	280	955
Am	35	46	50
V8	5	240	–
KS	124	614	875

### Acknowledgments

Financial support from specific university research (MSMT No 20-SVV/2016) and The Technology Agency of the Czech Republic (TH01030287) is gratefully acknowledged.



# POLY(METHYLENE BLUE) MODIFIED GRAPHITE ELECTRODES FOR THE ELECTROCATALYTIC OXIDATION OF HYDROGEN SULFIDE

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Electrode surface modification can improve the electrocatalytic activity towards analyte by facilitating the charge transfer reaction. Using an appropriate mediator immobilized on the electrode surface can protect it against passivation and even can change the electrochemical reaction mechanism.

Electrodes chemically modified by polymeric films have attracted considerable interest over the past two decades due to their potential application in electrocatalysis and electroanalysis. Electrochemical polymerization is one of the most common and useful techniques to obtain polymer thin film onto electrode surface. Compared to the chemical preparation of polymeric films it has some advantages, such as high reproducibility, thickness control and simple preparation methodology. Electrosynthesized polymers exhibit some unique behavior that the corresponding monomers do not always display.

In the past few years, surface-modified electrodes based on the electropolymerization of various phenoxazine and phenothiazine derivatives have been reported in the literature [1,2]. The electrocatalytic activity of poly(methylene blue) (pMB) in presence of some biologically active compounds has been already reported in several studies [3-7].

This work deals with electrochemical study of methylene blue (MB) polymerization process as well as characterization of deposited conductive film on two carbon-based substrates, basal plane highly oriented pyrolytic graphite (HOPG) and pencil-graphite electrode (PGE). Poly(methylene blue) modified electrodes (HOPG/pMB and PGE/pMB) have been prepared by potential cycling in aqueous electrolyte solution containing methylene blue monomer. It has been found that electrochemical properties and electrocatalytic activity of deposited film are greatly influenced by the type of electrode substrate. The modified electrodes exhibit electrocatalytic activity towards SH<sup>-</sup> group.

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# ROTATING ROD AS AN ALTERNATIVE TO ROTATING DISK ELECTRODE FOR HIGH TEMPERATURE APPLICATIONS

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Rotating disk electrode (RDE) is a useful tool for determination of electroactive species transport parameters and study of electrochemical reaction kinetics. Surface of the disk can be easily modified with various thin-films enabling catalyst characterization. One of the limiting factors of the RDE application is operating temperature range. Due to a low mechanical integrity, between the disk and its insulation, commercially available RDE's can be utilized only up to 80 °C. Contrary to this fact, vast portion of electrochemical processes operate at higher temperatures. Therefore, accurate evaluation of studied parameters at corresponding conditions is often rather problematic. To solve this problem an alternative type of RDE was proposed and tested in this work – rotating rod electrode (RRE).

In principle, RRE is made of electron conductive material without insulation on sides. Such arrangement enables its application in high temperature systems. On the other hand, the missing insulation limits effective application of the RRE to thin-film technique since the sides of RRE are also active parts of the electrode. Concerning these perquisites, RRE is an ideal solution for characterization of catalysts at electrolyte temperatures over 80 °C. However, change in electrolyte flow hydrodynamics in vicinity of electrode in comparison with the RDE is to be expected. Despite the RRE potential benefits no application related to catalyst characterization has been published yet.

The goal of this work comprised both experimental and theoretical evaluation of differences between the RDE and the RRE electrolyte hydrodynamics with respect to the electrolyte density and viscosity. The experimental data were obtained in  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  alkaline solution with various amount of glycerine added (in order to change viscosity) using glassy carbon RDE and RRE electrodes. These results were compared with 3D mathematical model developed in COMSOL Multiphysics 5.2. The experimental and the model data exhibited good agreement and showed unexpected dependence of the correlation factor between RDE and RRE on the electrolyte viscosity. An application of the RRE to the thin-film characterization of Pt/C catalysts for fuel cell application was successfully demonstrated at both ambient and elevated temperatures.

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# EFFECT OF SUBSTRATE HYDROPHOBICITY ON THE ELECTROCATALYTIC BEHAVIOUR OF WATER SOLUBLE PHTHALOCYANINE DERIVATE

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Metallophthalocyanine complexes are extensively studied for many potential applications and are known to be effective homogeneous and heterogeneous catalysts for a wide range of target species [1]. In addition they are commercially available and it is possible easily changes their properties by the substituting the ring or replacement of the central metal.

Metallophthalocyanine complexes are able to form films on different types of electrode substrates, for example: gold [2], carbonaceous materials such as carbon paste [3], glassy carbon [4], highly oriented pyrolytic graphite [5], and carbon nanotubes [6]. The immobilization of the active redox mediator can be achieved in various ways such as potential cycling methods [7], drop casting [8], spin coating [9], and mixing with carbon paste [10].

The water soluble *N,N',N'',N'''*-tetramethyltetrapyridinoporphyrazines are the quarternized derivates of phthalocyanines. These complexes are known to exist as monomers in solution without tendency to aggregation which limits the catalytic activity in aqueous solutions.

In this work, we describe how hydrophobicity of the electrode substrate affects electrocatalytic activity of water soluble non-aggregation *N,N',N'',N'''*-tetramethyltetra-3,4-pyridinoporphyrazinocobalt mediator. We focused on hydrophobic highly oriented pyrolytic graphite (HOPG) as well as hydrophilic annealed gold electrode (Au111). The immobilization of mediator has been carried out spontaneous adsorption from aqueous solution on electrode surfaces.

Hydrogen was selected as model analyte and the electrocatalytic activity of molecular film to hydrogen in aqueous solution has been investigated. For this purpose, electrochemical, *in situ* spectroelectrochemical, and *ex situ* microscopically characterizations have been performed. The detailed comparison of surface morphology, roughness parameters, thickness of deposited layers of mediator, and pH solution has been studied. The information obtained in this study is aimed at providing a more complete picture of the water soluble porphyrazine assembly on both hydrophilic and hydrophobic surfaces and investigating whether mediator can be used to hydrogen sensing.

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