



**UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE**

New trends in photo and electro catalysis

Proceedings of the 9th Czech-Austrian workshop

Josef Krýsa
EDITOR

20th May - 23rd May 2019

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 2nd workshop was held in December 2008 in Telč. Then the 3rd, 4th, 5th and 6th workshops were held in Hnanice in autumns 2009, 2011, 2012 and 2013, respectively. The 7th Czech - Austrian workshop was held in Hnanice in spring from 25th to 27th May 2015 and the last, 8th Czech - Austrian workshop was held in Hnanice in autumn from 30th November to 2nd December 2016.

The 9th Czech - Austrian workshop „New trends in photo and electro catalysis“ is held in Hnanice, Czech Republic from 20th May to 23rd May 2019. Proceedings from the workshop contain abstracts of contributions and are printed before the workshop. Participants are from four Czech institutions: University of Chemistry and Technology, Prague; Jaroslav Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic; Faculty of Chemical Technology, Technical University Brno and Technical University Ostrava, two Austrian institutions: Vienna University of Technology and University of Salzburg and one Slovak institution: Slovak University of Technology in Bratislava.

The objective of the workshop is, 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.

There is a longer delay between 8th and 9th workshop than previously expected (2.5 years). But on the other side there is significantly higher number of participating PhD students, almost all attend the workshop for the first time. This year we have also several undergraduate students from UCT Prague at the workshop. We believe that the workshop will be useful for all attendees and especially for PhD and undergraduate students who could present their results at the international forum.

Josef Krýsa and Guenter Fafilek

Acknowledgement

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9th Czech-Austrian workshop: New trends in photo and electro catalysis

CONFERENCE PLACE: HOTEL HAPPY STAR, HNANICE, CZECH REPUBLIC

(www.hotelhappystar.cz)

Date: 20th May - 23rd May 2019

Main Czech partner:

University of Chemistry and Technology, Prague - Prof. Dr. Ing. Josef Krýsa

Main Austrian partner:

Vienna University of Technology - Assoc. Prof. Dr. Guenter Fafilek

List of participants

Austria

Vienna University of Technology

Prof. Ulrika Diebold

Prof. Dominik Eder

Dr. Andreas Brueger

Dr. Martin Setvin

Dr. Alexey Cherevan

MSc. Sreejith Nandan

MSc. Jasmin Schubert

Ing. Jiří Pavelec



Ing. Michaela Plevová

Tomáš Imrich

Jakub Rusek

Anna Kloužková

J. Heyrovský Institute of Physical Chemistry AS CR

Prof. RNDr. Ladislav Kavan, DSc.

Ing. Pavel Janda, CSc.

Ing. Hana Krýsová, Ph.D.

RNDr. Markéta Zukalová, Ph.D.



University of Salzburg

Prof. Dr. Oliver Diwald

MSc. Juan Miguel Jiménez Morales

Dipl.- Chem. Ellie Neige

Dipl.- Ing. Valerie Werner



Brno University of Technology

Prof. Ing. Michal Veselý, Ph.D.

Doc. Ing. Petr Dzik, Ph.D.

Ing. Tomáš Svoboda

Ing. Kateřina Sýkorová



Czech Republic

University of Chemistry and Technology Prague

Prof. Dr. Ing. Karel Bouzek

Prof. Dr. Ing. Josef Krýsa

Dr. Michael Neumann-Spallart

Ing. Michal Baudys, Ph.D.

Ing. Šárka Paušová, Ph.D.

Ing. Michal Carda

Ing. Karel Denk

Ing. Martin Ďurovič

Ing. Adam Giurg

MSc. Lucia Pacileo



Technical University Ostrava

Prof. Ing. Kamila Kočí, Ph.D.

Prof. Ing. Petr Praus, Ph.D.

Ing. Miroslava Edelmannová

Ing. Aneta Smýkalová

Other countries

Slovak University of Technology in Bratislava, Slovakia

Prof. Ing. Vlasta Brezová, DrSc.

Doc. Ing. Dana Dvoranová, Ph.D.

Ing. Zuzana Barbieriková, Ph.D.



Programme

Monday, 20th May

11.00 – 13.00 arrival

13.00 – 13.30 registration of participants

13.30 Welcome talk (Josef Krýsa)

Chair: Josef Krýsa

13.40 Ulrike Diebold

BRIDGING ULTRAHIGH VACUUM SURFACE SCIENCE AND ELECTROCHEMISTRY: A FIRST STEP

14.10 Vlasta Brezová, D. Dvoranová, Z. Barbieriková, M. Mazúr

CAN C_3N_4 FULFILL OUR DREAM OF AN EFFICIENT VISIBLE-LIGHT ACTIVE PHOTOCATALYST?

14.40 Zuzana Barbieriková, T. Hajdu, V. Brezová, G. Žerjav, P. Djinović, A. Pintar

PROMISING TiO_2 - Bi_2O_3 COMPOSITE PHOTOCATALYST – EPR STUDY

15.00 Ellie Neige, Thomas Schwab, Gregor Zickler, Oliver Diwald

TiO_2 AND $BaTiO_3$ NANOPARTICLES: GAS PHASE FUNCTIONALIZATION AND SEPARATION OF PHOTOGENERATED CHARGES

15.20 – 15.45 coffee break

Chair: Ulrike Diebold

15.45 Ladislav Kavan

PEROVSKITE PHOTOVOLTAICS: INPUTS FROM ELECTROCHEMISTRY

16.15 Martin Setvin, I. Sokolovic, Z. Wang, M. Reticioli, M. Schmid, C. Franchini, U. Diebold

SURFACE STRUCTURE AND REACTIVITY OF CUBIC PEROVSKITES

16.35 Pavel Janda, H. Tarábková, J. Klíma

GASEOUS NANOBUBBLE ASSEMBLIES ON WATER-IMMERSED SOLID SURFACES

17.00 Hana Krýsová, J. Krýsa, L. Kavan

TiO_2 THIN FILMS WITH BLOCKING FUNCTION FOR APPLICATIONS IN SOLAR CELLS

17.25 End of the session

19.00 Common dinner

Tuesday, 21st May

Chair: Michal Veselý

9.00 Dana Dvoranová, V. Brezová, Z. Barbieriková, D. M. Tobaldi, M. Saeli
EPR STUDY OF PHOTOINDUCED PROCESSES OF NOBLE-METAL DECORATED
TITANIUM DIOXIDE PHOTOCATALYSTS

9.25 Juan Miguel Jiménez Morales, T. Berger
HYDROGEN DERIVED ELECTRON CENTERS IN TiO₂: REACTIVITY AND IMPACT ON
PHOTOELECTRODE PERFORMANCE

9.45 Jakub Rusek, Š. Paušová, J. Krýsa
TiO₂ NANOTUBULAR PHOTOELECTRODES: PREPARATION AND PROPERTIES

10.00 Alexey Cherevan, Dominik Eder et al.
EXPLORING NEW MATERIAL COMBINATIONS FOR PHOTOCATALYTIC WATER
SPLITTING

10.20 – 10.50 coffee break

Chair: Vlasta Brezová

10.50 Michal Baudys, J. Krýsa
PHOTOCATALYTIC REMOVAL OF NO_x ON TiO₂/ACTIVE CARBON COMPOSITE
PHOTOCATALYST

11.10 Andreas Brüger, G. Fafilek,
INFLUENCE OF VOLATILISATION ON THE OXIDATIVE TREATMENT OF CYANIDE
WASTE ILLUSTRATED BY PHOTOELECTROCATALYTIC DEGRADATION USING
TiO₂

11.30 Miroslava Edelmannová, L. Dubnová, M. Zvolská, I. Troppová, L. Matějová, M. Reli,
H. Drobna, P. Kuśtrowskic, L. Čapek, K. Kočí
N-La/TiO₂ PHOTOCATALYSTS FOR PHOTOCATALYTIC DECOMPOSITION
OF METHANOL – WATER SOLUTION

11.50 Lucia Pacileo, Š. Paušová, J. Krýsa
COMPOSITE CATALYSTS BASED ON TiO₂ FOR WATER TREATMENT

12.05 Adam Giurg, M. Paidar
STUDY OF DEGRADATION MECHANISMS IN THE CAPACITIVE DEIONIZATION
TECHNOLOGY

12.25 End of the session

13.00 Lunch

14.00 – 18.00 Individual discussions

19.30 Common dinner

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

Wednesday, 22nd May

Chair: Karel Bouzek

9.00 Markéta Zúkalová, Jan Procházka

MORPHOLOGY OPTIMIZATION OF $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ CATHODE MATERIAL FOR 48 V 3D Li-ACCUMULATOR

9.25 Michal Carda, D. Budáč, M. Paidar, K. Bouzek

OXYGEN ELECTRODE DEGRADATION AND REACTIONS KINETIC PARAMETERS IN REVERSIBLE SOLID OXIDE CELL

9.45 Aneta Smýkalová, Jan Storch, Jaroslav Žádný, Petr Praus

PREPARATION OF SUPHUR DOPED GRAPHITIC CARBON NITRIDE USING DIFFERENT TECHNIQUES

10.05 Anna Kloužková, M. Baudys, J. Krýsa

PREPARATION AND PROPERTIES OF PHOTOCATALYTICALLY ACTIVE TiO_2 – SiO_2 COATINGS

10.20 – 11.50 coffee break

Chair: Michael Neumann-Spallart

10.50 Šárka Paušová, M. Neumann-Spallart, J. Krýsa

Mo-BiVO_4 PHOTOANODES MODIFIED BY Co-Pi FOR PHOTOELECTROCHEMICAL APPLICATION

11.10 Tomáš Imrich, M. Neumann-Spallart, J. Krýsa

Fe_2O_3 BASED SEMICONDUCTOR PHOTOANODES FOR LIGHT ASSISTED WATER ELECTROLYSIS

11.25 Valerie Werner, S. Pokrant

SCALABLE PHOTOANODES FOR PHOTOELECTROCHEMICAL WATER-SPLITTING

11.45 Michaela Plevová, J. Hnát, J. Žitka, M. Paidar, K. Bouzek

CATALYST COATED MEMBRANE - NEW APPROACH IN THE ALKALINE WATER ELECTROLYSIS PROCESS

12.05 Martin Ďurovič, J. Hnát, K. Bouzek

NiCoP_x CATALYST FOR ELECTROCHEMICAL WATER SPLITTING: ACTIVITY AND STABILITY UNDER THE ALKALINE WATER ELECTROLYSIS CONDITIONS

12.25 Karel Denk, A. Giurg, M. Paidar

ELECTROCHEMICAL REMOVAL OF ORGANIC POLLUTANTS FROM PROCESS WATER

12.45 End of the session

13.00 Lunch

Chair: Ladislav Kavan

14.30 Key note talk I

T. Berger, N. Siedl, M. Niedermaier, T. Schwab, Oliver Diwald

LIGHT INDUCED CHARGE SEPARATION AND COMPETITIVE DEACTIVATION
PROCESSES IN METAL OXIDE NANOSTRUCTURES

15.15 – 15.30 coffee break

15.30 Key note talk II

Karel Bouzek, R. Kodým, M. Drakselová, M. Paidar

FLOW - FIELD GEOMETRY AND ITS IMPACT ON THE PEM FUEL CELL
PERFORMANCE

16.15 Final remarks

18.30 Closing dinner

Thursday, 23rd May

9.00 – 10.30 Check out from the hotel, departures

BRIDGING ULTRAHIGH VACUUM SURFACE SCIENCE AND ELECTROCHEMISTRY: A FIRST STEP

Ulrike Diebold

Institute of Applied Physics, TU Wien, Wiedner Hauptstrasse 8-10/134, 1040 Vienna, Austria

Transition metal oxides are promising materials for photo- and electrocatalysis. For a molecular-scale understanding of the underlying mechanisms and processes, experiments on well-characterized samples are necessary, i.e., specific facets of single crystals with a known composition, geometry and defect structure. Here the advanced methods of surface science, particularly Scanning Probe Microscopy (SPM) with atomic resolution, Thermally Programmed Desorption (TPD) with accurately-determined coverages, and X-ray Photoelectron Spectroscopy (XPS) with high resolution, together with first-principles computations based on Density Functional Theory (DFT) give unique insights. Bridging the gap to a (photo-)electrochemical environment is challenging, however.

In the talk we will address a first question, namely whether the atomic structure of oxide surfaces – once it is well-established in Ultrahigh Vacuum (UHV) – survives the exposure to liquid water. We use a novel apparatus that allows us to expose UHV-prepared samples to liquid water without exposure to air [1]. We find that the $\text{TiO}_2(110)$ surface maintains its (1x1) termination and that a (2x1) superstructure that is typically observed after water exposure in air stems from an ordered layer of carboxylates [2]. In contrast, the $\text{TiO}_2(011)$ -2x1 reconstruction is lifted upon exposure to liquid water, and the surface is fully hydroxylated [3]. The $(\sqrt{2}\times\sqrt{2})\text{R}45^\circ$ reconstruction [4] of the $\text{Fe}_3\text{O}_4(001)$ surface is also lifted in water, but the change proceeds slowly together with the growth of an oxy-hydroxide phase with a self-limiting coverage of 0.4 monolayers. Fe_3O_4 was also tested for OER in alkaline conditions, and found to be stable at the nanoscopic scale, with a facet-dependent reactivity [5].

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CAN C₃N₄ FULFILL OUR DREAM OF AN EFFICIENT VISIBLE-LIGHT ACTIVE PHOTOCATALYST?

V. Brezová, D. Dvoranová, Z. Barbieriková, M. Mazúr

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic.

The polymeric C₃N₄-based materials exhibit unique surface characteristics and semiconducting properties, and their application in the field of catalysis and photocatalysis has become a challenging yet emerging area of research [1]. Theoretical calculations considering the tri-*s*-triazine-based structure of *g*-C₃N₄ revealed the suppressed inter-triangle electron conduction evoking almost independent behaviour of each triangle and indicated the edge and middle nitrogen atoms as the centres of the hole-mediated reactions. The photoexcited electron is localized at the middle nitrogen and surrounding carbon atoms with hybridized orbitals resulting in the limited spatial separation of the photogenerated charge carriers [2]. The real C₃N₄-based photocatalysts contain a variety of the residual chemical defects in the crystal structure, which can serve as the surface or bulk sites for charge carrier trapping, with a substantial impact on the charge carriers dynamics and on the photocatalytic performance of these materials.

The paramagnetic centres of C₃N₄-based nanopowders prepared by the thermal condensation of melamine (MCN) with subsequent thermally etching (MCN-TE) and H₂O₂-treatment (MCN-H₂O₂ and MCN-TE-H₂O₂) were investigated using EPR spectroscopy in the dark, as well as upon UVA and visible-light photoactivation. Before exposure, the X- and Q-band EPR spectra of MCN and MCN-TE samples exhibit mainly the Lorentzian single-line of the electrons in the localized π -states in the C₃N₄ matrix ($g = 2.003$), revealing only an increased signal intensity in the case of thermally etched material due to the higher concentration of nitrogen vacancies. The complex Q-band EPR spectra obtained for MCN-H₂O₂ and MCN-TE-H₂O₂ were interpreted considering the presence of paramagnetic centres in the proximity of a heteroatom and nitroxide radicals produced *via* H₂O₂ interaction with C/N sites in the C₃N₄ polymeric network. Both the UVA and VIS-light irradiation of all powdered samples at 100 K lead to an increase in the intensity of the single line at $g = 2.0033$ indicating the photoinduced generation of the electrons in the localized states, as the EPR integral intensity of the corresponding signal decreased by the raised temperature (100–180 K) according to Curie law. The ability of the photocatalysts to generate the non-persistent radical species upon UVA or VIS-light exposure when dispersed in water or DMSO/water mixed solvent was tested by the spin trapping technique and by the elimination of nitroxide radical Tempol. The highest activities in the spin-adduct production of non-persistent radical species as well as Tempol scavenging were found for the thermally etched (MCN-TE) and pristine (MCN) photocatalysts [3].

Acknowledgements

This study was financially supported by Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0026/18). E.I. García-López and G. Marci are gratefully acknowledged for synthesis of C₃N₄-based photocatalysts.

References

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PROMISING TiO₂-Bi₂O₃ COMPOSITE PHOTOCATALYST – EPR STUDY

Z. Barbieriková^a, T. Hajdu^a, V. Brezová^a, G. Žerjav^b, P. Djinović^b, A. Pintar^b

^a Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

^b Department of Environmental Sciences and Engineering, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

Utilization of nanocrystalline semiconductors in the heterogeneous photocatalysis in terms of environmental water/air remediation is connected with high demands on the performance and stability of the photocatalyst. One of the recent strategies to meet these requirements represents the concept of a composite material, which can combine the advantages of two or more semiconductors and in the best-case scenario a synergic effect boosting the overall photocatalytic activity can occur. This motivated the efforts to combine anatase as the most active TiO₂ polymorph excelling in the proper balance between its surface chemistry-related properties and efficient light triggered charge carriers formation, with the bismuth oxide, a semiconductor not exhibiting as prominent characteristics as TiO₂, however possessing the band gap energies in the visible light region [1]. A series of composite TiO₂-Bi₂O₃ nanomaterial was prepared to achieve a highly active photocatalyst responsive to visible light due to a semiconductor heterojunction formation [2].

The assessment of the photocatalytic activity and the unravelling of the primary photoinduced processes are coupled with the formation of reactive sites in the material and reactive radical intermediates on its surface upon photoexcitation. Application of the electron paramagnetic resonance spectroscopy by the characterisation of these processes either in solid phase or in suspension can provide valuable information. The character and amount of reactive radical intermediates generated can be linked to the structural and morphological characteristics of the material, experimental conditions (solvent, presence of oxygen, etc.) and the type of irradiation source. EPR spin trapping technique enables the *in situ* monitoring of photogenerated non-persistent radical intermediates *via* their trapping by the reaction with the spin trapping agent, e.g. 5,5-dimethyl-1-pyrroline *N*-oxide, forming the corresponding spin adducts traceable by EPR [3].

Comprehensive EPR spin trapping experiments confirmed a highly beneficial effect of the combination of TiO₂ and Bi₂O₃ in the composites, as higher concentrations of spin adducts were monitored upon the UVA and visible-light photoexcitation of the composites compared to pure anatase sample as well as P25 benchmark suspended in water or dimethylsulfoxide, respectively. Even though the surface area of composites was lower than in the case of pure TiO₂, the formation of p-n junction between the n-type (TiO₂) and p-type (Bi₂O₃) semiconductors provided an effective separation of the photogenerated charge carriers, which can be further involved in the reactions on the surface. A remarkably high photocatalytic activity upon UVA exposure together with an observable visible light response demonstrates a strong potential of the studied composites to be utilized in the solar-light induced photocatalytic processes.

Acknowledgement

This work was supported by the Scientific Grant Agency of the Slovak Republic (Project VEGA 1/0026/18). G. Žerjav, P. Djinović and A. Pintar gratefully acknowledge the Slovenian Research Agency (ARRS) for financial support through Research Program No. P2-0150.

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TiO₂ AND BaTiO₃ NANOPARTICLES: GAS PHASE FUNCTIONALIZATION AND SEPARATION OF PHOTOGENERATED CHARGES

Ellie Neige, Thomas Schwab, Gregor Zickler, Oliver Diwald

Department of Chemistry and Physics of Materials, Paris-Lodron Universität Salzburg, Jakob-Haringer-Strasse 2a, A-5020 Salzburg, Austria.

Photocatalytic hydrogen production continues to be an attractive approach for the generation of a carbon-free energy supply. However, the efficiency of the solar energy conversion process is mainly limited by the recombination of photogenerated electron-hole pairs in the photocatalytic material along with the back-reaction of the intermediate species.[1] It was shown that the use of a ferroelectric metal oxides in combination with a photocatalytic materials components enhance the charge carrier lifetimes and promotes spatially selective photochemical reactions at the surface of the ferroelectric material.[2]

Here, we aim at an evaluation of charge separation properties of BaTiO₃ nanoparticles where ferroelectric polarization effects may enhance charge separation and, hence, diminish the recombination of photogenerated charges. For this reason, we compared vapor phase grown TiO₂ nanoparticles with BaTiO₃ nanoparticles from Flame Spray Pyrolysis and of comparable size distribution. In another step we produced nanocomposites of titanium dioxide (TiO₂) nanoparticles that are coated with barium, barium oxide or a barium titanate phase. In addition to the structural analysis via X-ray diffraction (XRD), we analysed structure and composition of particles and particle interfaces between the different materials components with transmission electron microscopy (EDX/ TEM).

Following this approach, we learned about the formation of a barium orthotitanate Ba₂TiO₄ phase that forms in deposits on top of the anatase nanoparticles. Local oxygen deficiencies, as determined by energy dispersive X-Ray spectroscopy (EDX), suggest the formation of TiO_{2-x} particles and point to local solid-solid and solid-vapor reactions that can be tracked on the single particle level. First results about the charge separation properties of the different particle powders, as characterized by quantitative photoexcitation induced charge separation experiments with electron paramagnetic resonance spectroscopy (EPR) will be discussed.[3]

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PEROVSKITE PHOTOVOLTAICS: INPUTS FROM ELECTROCHEMISTRY

L. Kavan

J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague 8, Czech Republic, E-mail: kavan@jh-inst.cas.cz

Though the first perovskite solar cell (PSC) reported in 2009, was an electrochemical (liquid-junction) device, there were few electrochemical studies during the next decade [1]. Electrochemistry can, nevertheless, provide salient inputs for the development of state-of-art PSCs' components. The vectorial charge-transfer over several interfaces in PSCs requires right alignment of conduction band minima (CBM) at the electron selective layer terminal and valence band maxima (VBM) at the hole-selective terminal, respectively. Furthermore the electron/hole selective layers should be compact (pinhole-free) to avoid recombination. All these properties can be characterized electrochemically. The electron-selective layer is usually made from TiO₂ or SnO₂ [2]. Amorphous ALD-made SnO₂ or TiO₂ films are pinhole-free for thicknesses down to several nm, but amorphous and crystalline ALD SnO₂ films substantially differ in their conduction band positions. The energy of CBM is usually measured by optical spectra (giving the band gap) and photoelectron spectra (XPS, UPS) providing VBM. Electrochemical alternative is the measurement of the flatband potential, which yields CBM, too. However, there is a considerable controversy between the electrochemical and vacuum (XPS, UPS) techniques concerning the position of CBM in TiO₂ (anatase, rutile, including the crystals with distinguished facets). A refined electrochemical analysis of single crystal TiO₂ electrodes (anatase, rutile, brookite) together with vacuum and near-ambient pressure XPS studies as well as theoretical (DFT) modelling points at the effect of interface influencing the CBM positions. Even 1-2 monolayers of water cause the relevant CBM shifts, which could explain these conflicts. Similar tasks are addressed at the positive (hole-selective) terminal of PSC. A promising hole-conductor to replace *spiro*-OMeTAD is CuSCN, particularly if it is interfaced to reduced graphene oxide (rGO). The natural p-doping of CuSCN is demonstrated by both Hall-effect and by Mott-Schottky plots in aqueous electrolyte solution. The corresponding flatband potentials (in V vs. Ag/AgCl) varied with the substrate type as follows: 0.12 (CuSCN@FTO), 0.08 (CuSCN@Au), -0.02 (CuSCN@glass-like-carbon) and 0.00 V (CuSCN@rGO). The acceptor concentrations determined from electrochemical impedance spectroscopy are by orders of magnitude larger than those from electrical conductivity and Hall effect. Raman spectra confirm that thiocyanate is the dominating structural motif over the isomeric isothiocyanate. In-situ Raman spectroelectrochemistry discloses substrate-specific intensity changes upon electrochemical charging. The blocking function of CuSCN is tested by a newly designed redox-probe, Ru(NH₃)₆^{3+/2+}. It has not only the appropriate redox potential for investigation of the CuSCN films, but also avoids complications of the standard 'ferrocyanide test' which is normally used for this purpose.

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SURFACE STRUCTURE AND REACTIVITY OF CUBIC PEROVSKITES

M. Setvin,^a I. Sokolovic,^a Z. Wang,^a M. Reticioli,^b M. Schmid,^a C. Franchini,^b U. Diebold^a

^a Institute of Applied Physics, TU Wien, Wiedner Hauptstrasse 8-10/134, 1040 Vienna, Austria

^b Faculty of Physics and Centre for Computational Materials Science, University of Vienna, Sensengasse 2, 1090 Vienna, Austria

Perovskite oxides are a broad class of materials with a wide range of technically relevant physical and chemical properties. They are interesting for applications like photo/electro/catalysis, fuel cells, electronics, spintronics or sensors, but their practical use is hindered by a lack of understanding their surface chemistry and by a limited stability of the material under operating conditions. Surface science traditionally explains mechanistic details of processes occurring at materials' surfaces, but perovskites appear particularly challenging for our field.

The ternary chemical composition of perovskites allow formation of many different terminations at one crystal plane. The centre of scientific interest lies in bulk-terminated perovskites, but these are difficult to prepare in a sufficient quality for atomically-resolved studies. We have developed a method for preparing such surfaces by ferroelectricity-assisted cleaving [1,2], and demonstrate it on the (001) planes of SrTiO₃ and KTaO₃. The combined non-contact Atomic force microscopy/Scanning tunnelling microscopy (AFM/STM) appears to be a key tool for atomic-scale characterization of these surfaces. We discuss the evolution of the surface structure and chemical properties with annealing, under exposure to water vapour, and in liquid water.

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GASEOUS NANOBUBBLE ASSEMBLIES ON WATER-IMMERSED SOLID SURFACES

P. Janda, H. Tarábková, J. Klíma

Department of Electrochemical Materials, J. Heyrovský Institute of Physical Chemistry, CAS,
Dolejškova 3, 182 23 Prague 8, Czech Republic

Surface gaseous nanodomains, represented mostly by gaseous nanobubbles residing on water-immersed solid surfaces, extend concept of binary solid-liquid interface to 3-phase solid-gas-liquid system, which existence is often not anticipated.

As gaseous nanodomains are relatively stable and their appearance density on solid-liquid interface may correspond up to 90% coverage of immersed surface, they bring significant uncertainty pattern to determination efficiency and kinetics of heterogeneous interfacial processes. The nanobubble research thus becomes important for various fields including heterogeneous (electro)catalysis, electrodeposition, charge storage, photochemical energy conversion, immersion lithography etc.

The assembly of surface gaseous nanodomains can vary from randomly distributed solitary nanobubbles to close-packed nanobubble arrangement - quasi-2D (liquid) nanofoam. It represents a special form of foam, which, unlike common foams occupying top of liquid, is composed from single-layer of gaseous nanobubbles pinned to immersed solid surface.

Forces at surface nanobubble ternary interface were found capable to rearrange immersed solid surfaces in a specific manner including room temperature exfoliation of graphite and nanostructuring on polymer surfaces. Research performed at the J. Heyrovský Institute of Physical Chemistry, in the Department of Electrochemical Materials is focused on surface nanobubble interactions with immersed solid surfaces leading to nanobubble-assisted nanostructuring and nanoporation^{1,3,4,6} of polymeric films and on nanobubble shielding effect in electrochemical deposition and adsorption processes.

Special attention is paid to nanobubble imaging by AFM in situ and to correlation of their arrangement with nanobubble-formed nanostructures on immersed solids^{2,5}.

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TiO₂ THIN FILMS WITH BLOCKING FUNCTION FOR APPLICATIONS IN SOLAR CELLS

H. Krýsová^a, J. Krýsa^b, L. Kavan^a

^a J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 2155/3, 182 23 Praha 8, Czech Republic, (hana.krýsova@jh-inst.cas.cz)

^b University of Chemistry and Technology, Prague, Technická 5, 166 28 Praha 6, Czech Republic

For the proper function of the solar cells, an ideal blocking layer must be pinhole-free and completely covering the relatively rough FTO surface. Back reaction of photoinjected electrons with the oxidized form of mediator or with the hole-transporting medium is an undesired parasitic process. It occurs both at the TiO₂ surface and at the naked F-doped SnO₂ conducting glass (FTO) areas which are uncovered by the titanium dioxide nanoparticles. This recombination current over the FTO is relatively small in a liquid-type DSC, but it becomes crucial in the SSDSCs as well as in the perovskite solar cells using the same architecture [1].

There are various techniques for blocking layer fabrication, mainly spray pyrolysis [2], magnetron sputtering, chemical vapour deposition technology and atomic layer deposition (ALD)[3].

The present work deals with several types of preparation of blocking TiO₂ films, their characterization and evaluation of electrochemical and photoelectrochemical properties crucial for their application as a blocking layer in solar cells. Blocking properties of the layers were tested by cyclic voltammetry with K₄[Fe(CN)]₆ / K₃[Fe(CN)]₆ as a model redox probe with simple one-electron-transfer reaction. Mott-Schottky analysis was used to obtain flat band potential and donor density, photoelectrochemistry for the evaluation of photocurrent response.

Very promising thin transparent blocking TiO₂ films, which exhibit both photoelectrochemical response and very good blocking properties, were prepared by semi-automatic spray pyrolysis of precursors consisting of diisopropoxy titaniumbis(acetylacetonate) as the main component [4]. The deposition temperature of 450°C is necessary for the fabrication of highly photoactive TiO₂ films. Blocking properties of the as deposited TiO₂ films (at 450°C) are impaired by post-calcination at 500°C, but this problem can be addressed by an increase in number of spray cycles. The modification of the precursor (by adding acetylacetone) results in the fabrication of TiO₂ films exhibiting perfect blocking properties which are not influenced by post-calcination.

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EPR STUDY OF PHOTOINDUCED PROCESSES OF NOBLE-METAL DECORATED TITANIUM DIOXIDE PHOTOCATALYSTS

D. Dvoranová^a, V. Brezová^a, Z. Barbieriková^a, D. M. Tobaldi^b, M. Saeli^b

^a Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

^b Department of Materials and Ceramics Engineering/CICECO – Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal.

Japanese word *Shibuichi* means “one-fourth” and represents a traditional dark grey alloy made from one part of silver and three parts of copper which is mostly used for the decoration of historical Japanese swords. *Shibuichi* became inspiration for the synthesis of noble-metal/metal-oxide (Ag and/or CuO) titania nanohybrids as potential materials for NO_x and VOCs removal upon solar radiation. Metallic nanoparticles are characterized by their strong interaction with resonant photons through the excitation of surface plasmon resonance which improves photocatalyst’s activity enabling the effective photoexcitation with UVA, as well as broad visible-light range [1]. The series of TiO₂ nanopowders decorated with Ag and/or Cu(II) containing various molar amounts of dopants (1-10 %) was investigated by means of EPR spectroscopy. The X-band solid-state EPR spectra at room and low temperature (100 K) were measured to follow the paramagnetic centers in the nanocrystalline photocatalysts before and upon UVA/visible-light photoactivation. The signals of paramagnetic Cu(II) ions dominate the EPR spectra of all copper-containing nanopowders limiting the detection of photogenerated trapped charge carriers. Consequently, the charge transfer processes upon photocatalysts photoexcitation were monitored also in their frozen dimethylsulfoxide (DMSO) suspensions, evidencing the formation of EPR signals attributed to alkyl radicals produced *via* interaction of photogenerated electrons and holes with DMSO (*e. g.* $\cdot\text{CH}_3$, $\cdot\text{CH}_2\text{SOCH}_3$) [2]. However, the expected decline of EPR signal of Cu(II) ions reflecting the one-electron reduction to diamagnetic Cu(I) species was only negligible, most probably due to their rapid re-oxidation *via* consecutive reactions with alkyl radicals generated in DMSO matrix. The production of paramagnetic species in the aerated DMSO suspensions upon UVA/visible-light exposure at room temperature was confirmed also by EPR spin trapping technique using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) [3]. The DMPO spin-adducts of photogenerated radicals correlated well with those produced upon photoexcitation of frozen DMSO matrix at 100 K, and DMPO-adduct concentration sensitively reflected the noble-metal character/concentration and loading of photocatalysts in the reaction system.

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HYDROGEN DERIVED ELECTRON CENTERS IN TiO₂: REACTIVITY AND IMPACT ON PHOTOELECTRODE PERFORMANCE

J.M. Jiménez^a, T. Berger^a,

^a Department of Chemistry and Physics of Materials, University of Salzburg, Jakob-Haringer Straße 2a, 5020 Salzburg, Austria

Hydrogen sources are ubiquitous during the synthesis, processing and application of metal oxide nanomaterials. The impact of hydrogen on both the physicochemical and the functional materials' properties needs therefore to be understood. [1] We studied the spectroscopic properties of electron centers generated at the solid/gas interface between anatase TiO₂ nanoparticle ensembles (powders or immobilized films) and atomic hydrogen using UV/Vis-, IR- and Electron Paramagnetic Resonance (EPR) spectroscopies. The reactivity of the electron centers towards water and oxygen was investigated. Finally, we aimed at elucidating whether hydrogen doping of anatase TiO₂ nanoparticle films at the solid/gas interface impacts on their macroscopic performance when being used as photoelectrodes for water oxidation in aqueous electrolytes.

Anatase TiO₂ nanoparticle powders ($d = 10 - 20$ nm) were produced by chemical vapor synthesis. Subsequently, the powder was thermally annealed ($T = 600$ °C) at high vacuum conditions ($p < 10^{-5}$ mbar) and in oxygen atmosphere ($p = 20$ mbar) to obtain clean and stoichiometric oxide surfaces. TiO₂ films were prepared by drop casting of aqueous particle slurries onto conducting glass substrates (fluorine-doped tin oxide) or a tungsten mesh and were subsequently annealed at 450 °C. Upon exposure of the anatase TiO₂ nanoparticle powders to atomic hydrogen at $T = 298$ K, Ti³⁺ centers are formed and evidenced by EPR- and UV/Vis-spectroscopies. A quantitative analysis yields ~ 1 spin per anatase TiO₂ nanoparticle. Ti³⁺ centers are stable upon H₂O addition ($p[\text{H}_2\text{O}] = 0.1$ mbar). However, electrons are transferred to oxygen both in the absence and in the presence of adsorbed water. IR spectra of anatase TiO₂ nanoparticle films evidence the presence of terminal OH-groups after sample activation. Their concentration does not change significantly upon sample exposure to atomic hydrogen. However, a monotonic absorption background appears between 4000-1000 cm⁻¹ and is attributed to delocalized electrons in the TiO₂ conduction band. The broad absorption background is preserved upon water addition ($p[\text{H}_2\text{O}] = 0.1$ mbar), however, disappears upon oxygen addition ($p[\text{O}_2] = 20$ mbar) both in the absence and in the presence of adsorbed water.

To study the impact of hydrogen doping on the electrochemical and photoelectrochemical film properties, a TiO₂/electrolyte interface was built up in a bottom-up approach. First, TiO₂ films were chemically reduced at high vacuum conditions. Then, a charged semiconductor oxide/electrolyte interface was generated by controlled water condensation onto the film followed by the addition of deaerated 0.1 M HClO₄ solution. Excess electrons generated at the solid/gas interface were then electrochemically extracted at the solid electrolyte interface. For anatase TiO₂ films the number of extracted electrons accounts for ~ 10 electrons per anatase TiO₂ nanoparticle. Upon UV-induced water oxidation, we observe a strong increase of the photocurrent (enhancement factor: 1.5 - 2), which fades away on a time scale of hours. We attribute the transient performance increase to accelerated charge transport and reduced recombination in hydrogen doped anatase TiO₂ electrodes. [2]

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TiO₂ NANOTUBULAR PHOTOANODES: PREPARATION AND PROPERTIES

J. Rusek^a, Š. Paušová^a, J. Krýsa^a

^a Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6

The resources of fossil fuels are limited and their use (e.g. combustion or energy release) has very often serious impact to environment (e.g. pollution of air and water). That is the main reason, why many researches look for the cleaner alternative energy sources and methods for cleaning of environment. Important source of alternative energy is sun. Electrode consisting of TiO₂ particles can be used as photoanode in dye-sensitized solar cells (DSSC) [1], where solar energy is converted to electrical energy or in photoelectrochemical cell where solar energy can be used for water treatment. Photoanode consisting of TiO₂ nanoparticles has high surface area but suffers from insufficient contact between particles resulting in slow electron transport through nanocrystalline structure and significant recombination. This negative effect can be suppressed by fabrication of TiO₂ photoanodes with 1-D (nanotubular) structure. The aim of this work is therefore the preparation and optimization of the titania nanotubular TNT photoanodes for possible application i) in DSSC and ii) for the photoelectrochemical decomposition of organic pollutants in water [2]. The TNT layers were produced by anodization of titanium foil. As-prepared TiO₂ nanotubes are amorphous, to get anatase crystalline structure it was necessary to use thermal treatment [3].

Crystallinity and morphology of the TNT layers were characterized by XRD and SEM. The key factor for the efficiency of the DSSC is the adsorbed amount of an organic dye on the TNT surface. Therefore, the adsorption of the model dye N719 ([*cis* – bis (isothiokyanato) bis (2,2' – bipyridyl – 4,4' – dikarboxylato) ruthenium (II)] bis – tetrabutylammonium) was studied by UV-Vis spectrophotometry [4]. Photocurrents of TNT photoanodes were, as the key parameter determining the efficiency of a photoelectrochemical oxidation of organic pollutants, measured by linear voltametry and chronoamperometry in aqueous electrolyte under illumination (solar light and monochromatic UV light). Furthermore, the values of the IPCE (Incident photon-to-current conversion efficiency) were determined. Anodization for 15, 45, 90 min results in TNT layers of thickness of 5.1, 7.4 and 10.5 μm, respectively. Photocurrents increase nonlinearly with increasing thickness of TNT layer up to 7.4 μm and for 7.4 and 10.5 μm photocurrents are almost the same. Amount of adsorbed dye N719 on nanotubular surface increases linearly with increasing thickness of TNT layers up to 7.4 μm (80.6 nmol/cm²), for higher thickness (10.5 μm) adsorbed amount of N719 dye decreases. Achieved results for nanotubular layers were compared with results for nanoparticle layers and further analysed considering the estimated surface area of both types of layers.

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PHOTOCATALYTIC REMOVAL OF NO_x ON TiO₂/ACTIVE CARBON COMPOSITE PHOTOCATALYST

M. Baudys^{a,b}, J. Krýsa^b

^a Technopark Kralupy, University of Chemistry and Technology Prague, Žižkova 7, 27801 Kralupy nad Vltavou, Czech Republic

^b Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6, Czech Republic.

Photocatalysis on TiO₂ represents promising method which can be applied in air treatment to decompose volatile organic compound in air. According to the standard ISO 22197, there are many methods of photocatalytic activity assessment based on removal of acetaldehyde, formaldehyde, toluene and NO_x [1]. Opposite to mineralization of organics, photocatalytic removal of NO_x is based on transformation of NO_x from gaseous phase to the form of nitrite/nitrate. Although NO is very quickly oxidized (eq. 1-2), potential accumulation of nitric acid causes production of NO₂ (eq. 3) [2]. Photocatalytic efficiency of test piece is than given as a sum of NO_x, which is equal to the difference between amounts of NO removed and amount of NO₂ produced by the test piece.



Addition of carbon material to TiO₂ photocatalyst in the form of graphene oxide or carbon nanodots can be used to improve electronic properties [3]. The addition of active carbon may concentrate chemical species in the vicinity of the semiconductor but it should also allow for desorption and transport of species to the semiconductor [4]. The objective of this contribution is to evaluate the influence of the addition of active carbon on the removal efficiency of NO_x.

Several AC materials differing with their texture properties and ratio of micro and mesoporous were used. First AC sample is produced by pyrolysis of coconut shells and exhibits specific surface area about 1600 m². According to the shape of N₂ isotherm it can be concluded that sample is not purely mesoporous but it contains small amount of micropores (6%). Second AC sample is also prepared by pyrolysis of coconut shells and exhibits BET surface area about 1700 m²/g and the content of micropores about 21%. Third sample is prepared by activation of coal, exhibits the smallest BET surface (only 900 m²/g) but the highest content of micropores (55%). Results of photocatalytic activity were expressed as amount of removed NO, NO_x and formed NO₂, respectively. Compared to pure TiO₂ the removal ability of composite photocatalysts is about 40 to 100 % higher depending on the BET surface area the content of micropores. Due to the presence of AC, majority of produced HNO₃ is adsorbed on the AC surface. This prevents the accumulation of HNO₃ on the surface of TiO₂ and reaction of HNO₃ with NO (eq. 3) to NO₂.

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INFLUENCE OF VOLATILISATION ON THE OXIDATIVE TREATMENT OF CYANIDE WASTE ILLUSTRATED BY PHOTOELECTROCATALYTIC DEGRADATION USING TiO_2 .

A. Brüger, G. Fafílek

Institute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164
A-1060 Vienna, Austria (email: brueger@tuwien.ac.at)

The loss of hydrogen cyanide in industrial and technological applications using cyanide is an important factor in the evaluation of cyanide consumption as well as the assumption of its toxicity. Threshold levels are set for hydrogen cyanide in view of its hazardousness. The levels though are found in a wide range from 10 ppm in workplace air averaged over an 8-hour workday and 40-hour workweek to 0.8 ppb for a continuous inhalation exposure to the human population without an appreciable risk of deleterious effects during a lifetime [1, 2].

Rationale for the definition of the threshold levels are influenced by investigations of cyanide depletion with ambiguous interpretations of the fraction of volatilised hydrogen cyanide. Neglecting HCN-volatilisation can lead to the assumption of an excessive oxidation rate of cyanide in the atmosphere and water or to an increased metabolism rate in humans [3, 4, 5]. As a consequence, some cyanide exposure limits need to be discussed and cyanide treatment results recalculated.

In our work we describe a method for the determination of hydrogen cyanide loss in photoelectrocatalytic experiments. The volatilised HCN is analysed considering the influence of the atmosphere surrounding the experimental setup. It can be shown that the degradation rate of cyanide increases with decreasing pH while at low pH the volatilised amount of hydrogen cyanide exceeds the oxidised fraction.

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N-La/TiO₂ PHOTOCATALYSTS FOR PHOTOCATALYTIC DECOMPOSITION OF METHANOL–WATER SOLUTION

M. Edelmannová^a, L. Dubnová^b, M. Zvolská^a, I. Troppová^a, L. Matějová^a, M. Reli^a, H. Drobná^b, P. Kuśtrowski^c, L. Čapek^b, K. Kočí^b

^a Institute of Environmental Technology, VŠB-Technical University of Ostrava, Ostrava – Poruba, Czech Republic

^b Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic.

^c Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland

Currently, a clean energy production from renewable sources is one of the most important challenges. Hydrogen is in the centre of attention as an ideal energy carrier for the future due to its great energy content in comparison with other fuels. Photocatalytic processes are one of the most promising ways to H₂ produce by utilizing the renewable sources such as solar energy. Nowadays, several strategies were developed to increase the photocatalytic activity of TiO₂ for production of hydrogen from water or water-alcohol mixtures [1].

N-La/TiO₂ materials were prepared with approximately the same amounts of La (0.14-0.16 wt. %) and different amounts of N (0.33-0.97 at. % of surface nitrogen). The physico-chemical and electronic properties of all synthesized photocatalysts were characterized by nitrogen physisorption, diffuse reflectance spectroscopy, X-ray powder diffraction, Raman spectroscopy and photoelectrochemical measurements. The prepared photocatalysts was investigated for photocatalysis in liquid phase for methanol photocatalytic decomposition for the first time. The photocatalytic decomposition of CH₃OH was realized in a homemade stirred batch reactor (volume 355 ml) with a suspended N-La/TiO₂ photocatalyst illuminated by the UV 8 W Hg lamp (peak light intensity at 365 nm wavelength) situated on the top of the quartz glass visor.

N-La/TiO₂ materials showed approximately the same specific surface area and crystallite size, with values ranging for La/TiO₂ and N/TiO₂ photocatalysts. The hydrogen yield increased in order of TiO₂ < La/TiO₂ < N/TiO₂ (0.46 at. %, < N-La/TiO₂ (0.33 at. %, 0.36 at. % and 0.97 at. % of N). It is evident that the N co-doping led to the increase of the photocatalytic behaviour of N-La/TiO₂ photocatalysts in contrast to TiO₂ and La/TiO₂. The highest amount of hydrogen was observed for 0.97 at. % N-La/TiO₂ which was 4 times higher in comparison with pure TiO₂. This result demonstrates that co-doping with non-metal and metal ions is more powerful to increase the photoactivity of TiO₂ than doping by single type of ion. For studied N-La/TiO₂ photocatalysts, the photocatalytic activity increased with the increasing amount of surface nitrogen (interstitial positions, XPS), and subsequently with increasing amount of oxygen vacancies (Raman spectroscopy) and decreasing amount of surface oxygen species (surface lattice O species and hydroxyl groups, XPS).

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COMPOSITE CATALYSTS BASED ON TiO₂ FOR WATER TREATMENT

L. Pacileo, Š. Paušová, J. Krýsa

Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6.

The titanium dioxide has many advantages and combined with AC has appeared as an important photocatalyst for removal of organic pollutants from the water [1]. A small amount of Activated Carbon (AC) should facilitate the adsorption of the organic molecules on the TiO₂ surface [2, 3].

This work deals with the development of composite photocatalytic materials, which could be applied in the water treatment. In particular, the photocatalytic activity of various composites containing TiO₂ (P25, Evonik, 70:30 anatase to rutile % w/w) and different types of Activated Carbon (AC0 from coconut shells and AC20 from coal) were investigated using aqueous solutions of Benzoic Acid (HBz) as a model compound (initial concentration of [HBz] = 1•10⁻⁴ mol/l).

Experiments under irradiation and in the dark (adsorption) were performed in a cooled, stirred batch reactor and the analyses were carried out using HPLC and UV-vis spectroscopy. The AC 's composite photocatalyst (of ratio AC/TiO₂ = 0.07 and 0.23), were prepared from as received AC or milled AC (using high frequency mill and different time of milling). Composite powder was then immobilised on glass substrates, mass of TiO₂ was 0.25, 0.5 or 1 mg TiO₂/cm².

The immobilised layers prepared from as received AC were unstable. After milling for 60 min, the particles size of AC changed from 50-70 to 3-20 µm for AC20 and from 20-100 to 9-40 µm for AC0. The decrease of particles size results in an increase of the stability of prepared layers and at the same time in an increase of HBz adsorption.

Immobilised composites showed high photocatalytic activity, for composite consisting of 60 min. milled AC20 (ratio AC/TiO₂ =0.23, 0.5 mg TiO₂/cm²), 50% of HBz was removed in 1 hour of UV irradiation, the complete HBz removal was reached in 150 minutes. The most stable and active composite layers were used repeatable for HBz removal, it was found that repeated removal takes place with the same efficiency.

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STUDY OF DEGRADATION MECHANISMS IN THE CAPACITIVE DEIONIZATION TECHNOLOGY

A. Giurg, M. Paidar

Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6, Czech Republic (giurga@vscht.cz)

Water treatment is a very important process for human life. The large amount of water has to be treated worldwide. The most ordinary methods for water treatment are distillation, reverse osmosis and electrodialysis at present time. Another promising process is capacitive deionization (CDI) intensively studied in recent years. CDI is a very simple process for salinity reduction of treated water. The key components of CDI are porous electrodes. Electrodes are usually made from carbon material. Electrodes have to exhibit high specific surface area, pore structure suitable for ions capturing, good mechanical properties and high electron conductivity. The presented work is focused to study of degradation mechanisms in the CDI and prolongation of lifetime of CDI technology.

Degradation of carbon electrodes is the most problematic in CDI technology. This degradation is very important for lifetime of CDI. Therefore it is necessary to find degradation mechanisms out because after it we can prevent or reduce degradation of the electrodes and improve lifetime of CDI technology. Electrode degradation can be caused by undesirable faradaic reactions or blocking of electrode surface. Faradaic reactions cause oxidation of carbon to carbon dioxide or modification of electrode surface (creation $-\text{OH}$, $=\text{O}$, $-\text{COOH}$). Blocking of electrode surface and decreasing of electrosorption capacity of electrodes is caused by precipitated compounds of Mg^{2+} and Ca^{2+} in the pores of electrodes.

Quantity of adsorbed and desorbed ions in one cycle from/to processed water saturated by air was decreasing very fast in the time whereas quantity of adsorbed and desorbed ions in the cycle from/to processed water saturated by nitrogen (minimum of oxygen) was decreasing significantly slower. Quantity of adsorbed and desorbed ions in the cycle from/to processed water increased after rinsing the CDI cell by hydrochloric acid. Therefore compounds of Mg^{2+} and Ca^{2+} were removed from the pores of the electrodes. Usually these compounds are precipitated in alkaline environment. It was confirmed in the batch cell that solution near a negative electrode is alkaline and near a positive electrode is acidic, and pH changes are more significant with present pure oxygen. Therefore occurrence of faradaic reactions in CDI cell is influenced by concentration of dissolved oxygen. Changes of pH were significant (approximately 3,5–10,5). Modification of electrode surface was confirmed by XPS. Arising oxygen on the positive electrode oxidized the surface of the electrode. The carboxyl groups on the surface of the electrode behave like ion-exchange resin. Adsorption and regeneration cycles were reversal after few hundreds hours of operation. After potential was applied, ions released from carboxyl groups and just few ions from water were adsorbed on the surface. And during regeneration phase, ions desorbed from electrode surface but more ions were captured on the carboxyl groups.

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MORPHOLOGY OPTIMIZATION OF $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ CATHODE MATERIAL FOR 48 V 3D Li-ACCUMULATOR

Markéta Zukalová^a, Jan Procházka^b

^aJ. Heyrovský Institute of Physical Chemistry, the Czech Academy of Sciences, Dolejškova 3, CZ-18223, Prague 8, Czech Republic

^bHE3DA, s.r.o., Beranových 130, CZ-19905 Prague 9, Czech Republic

The layered $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) is a promising cathode material and represents environmentally acceptable replacement of widely used LiCoO_2 [1]. NMC is isostructural to layered LiCoO_2 , its Co content is only 1/3 of that in LiCoO_2 and exhibits impressive stability upon cycling, reasonable specific capacity (150 mAh/g) and good high rate capability. Due to relatively low Li^+ diffusion coefficients of the order of 10^{-10} - 10^{-15} cm^2/s [2] NMC material consisting of nanocrystals with well-developed structure represents the best candidate for stable and fast Li-ion battery.

We prepared a series of nanocrystalline NMC samples by appropriate treatment of commercial NMC material. All the studied samples treated by calcination exhibited stable and reproducible electrochemical behavior. Raman analysis of the samples after galvanostatic cycling did not prove pronounced structural changes[3]. Optimized samples provided charge capacity of 141 mAh/g (cyclic voltammetry) and 144 and 135 mAh/g (galvanostatic chronopotentiometry) at 1 and 10C, respectively and was used as a cathode material in the basic unit of 48 V accumulator - 4 V cell with 100 Wh capacity and excellent cycling stability.

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OXYGEN ELECTRODE DEGRADATION AND REACTIONS KINETIC PARAMETERS IN REVERSIBLE SOLID OXIDE CELL

M. Carda, D. Budáč, M. Paidar, K. Bouzek

Department of Inorganic Technology, University of Chemistry and Technology, Prague, Technická 5, 16628 Praha 6, Czech Republic

The high-temperature approach with a solid oxide electrolyte, the so-called solid oxide cells (SOCs), in combination with renewable energy sources and high potential heat, represents a promising method of clean hydrogen production for the intermittent storage of electrical energy. [1] SOCs offers significant advantages for hydrogen production over other similar technologies. This is mainly the consequence of high operating temperature (700 – 900 °C), which leads to fast electrodes kinetics, the possibility to operate in reversible modes (electrolysis – EC or fuel cell – FC) within a single cell; however, the high temperature also enhances degradation processes [2]. Particularly the interface contact degradation of electron/ion conductive phase contact at an oxygen electrode has a great impact on SOCs overall performance.

The oxygen evolution or reduction reaction (OER/ORR) is mainly responsible for cell activation losses; therefore, minimalization of activation or ohmic losses at the oxygen electrode is decisive for stable and high performance of SOCs. Therefore, a thorough understanding of the electrochemical reaction and structural characteristics of the oxygen electrode-electrolyte interface is needed. Electrode conductive material $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-x}$ (LSM) and ion conductive material $\text{ZrO}_2 - 8 \text{ mol.}\% \text{ Y}_2\text{O}_3$ (YSZ) are commonly used materials as oxygen electrode in SOCs. Hence, a series of SOCs consisting of YSZ electrolytes with screen printed LSM electrode and Ni-based hydrogen electrode was prepared. To investigate initial up-to-date SOCs systems stability, each LSM-YSZ-Ni cell was tested at first in FC and then in EC mode for 300 h in potentiostatic mode. After several days in either mode, degradation of cell was observed. Therefore, symmetrical LSM-YSZ-LSM cells were prepared to examine degradation mechanisms and kinetics of OER and ORR under different O_2 partial pressures and temperatures. Each cell was examined by various electrochemical methods and the structural changes at the interface were examined by postmortem SEM and XRD analysis.

Results indicate that during an operation at 700 °C only a slight increase in polarization and ohmic losses was observed; however, at 800 °C the ohmic losses increased rapidly. SEM analysis suggested no visible morphological changes at the interface; however, XRD analysis showed the development of a new nonconductive phase at the interface. Corresponding kinetic parameters of oxygen electrode reactions experimental data were interpreted by means of Butler-Volmer equation. Acquired kinetics parameters suggest that they are dependable on adsorption and desorption of reactants and products respectively. Overall, our results broaden the knowledge of OER and ORR kinetics at LSM electrode and long-term tests indicate loss of LSM-YSZ interface.

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PREPARATION OF SULPHUR DOPED GRAPHITIC CARBON NITRIDE USING DIFFERENT TECHNIQUES

Aneta Smýkalová^a, Jan Storch^b, Jaroslav Žádny^b, Petr Praus^a

^a Institute of Environmental Technology, VŠB-Technical University of Ostrava, 17. listopadu 2172/15, 708 00 Ostrava-Poruba, Czech Republic

^b Institute of Chemical Process Fundamentals of the CAS v.v.i., Rozvojová 135/1, 165 02 Praha-Lysolaje, Czech Republic

Recently, graphitic carbon nitride (g-C₃N₄) has attracted an attention due to its extraordinary chemical and thermal properties and photoactivity under visible light (band-gap energy of 2.7 eV). However, its photocatalytic applications are limited by fast recombination of photoinduced electrons and holes. A non-metal doping of the g-C₃N₄ structure seems to be an effective strategy to obtain g-C₃N₄ based materials with enhanced photocatalytic activity suitable for decomposition of organic pollutants in waters [1].

Sulphur-doped g-C₃N₄ (S-g-C₃N₄) can be obtained by two different ways. The first way of the g-C₃N₄ doping can be performed by direct calcination of melamine and S-containing precursors. The second way consists in derivatization of already prepared g-C₃N₄ with some reactive S-containing compounds. The S-g-C₃N₄ direct synthesis was realized by the calcination of pure thiourea, melamine and thiourea, melamine and trithiocyanuric acid and pure trithiocyanuric acid. The g-C₃N₄ derivatization was carried out by the reactions of bulk and exfoliated g-C₃N₄ with H₂SO₄, NH₂SO₃H, MeSO₂Cl/Et₃N, ClSO₃H/Et₃N and SOCl₂/Et₃N. Bulk g-C₃N₄ was synthesized by thermal treatment of melamine at 550°C and exfoliated by heating of bulk g-C₃N₄ at 500°C [2].

The prepared materials were characterized by common instrumental methods, such as UV-VIS DRS, FTIR, XRD, SEM, TEM, BET measurements etc. Their photocatalytic activity was evaluated by the decomposition of Acid Orange 7 (AO7) under UVA irradiation with the maximum intensity at 368 nm. The most active photocatalyst was prepared by the derivatization of bulk g-C₃N₄ with MeSO₂Cl. The 91% photodecomposition of AO7 was achieved after 2 hours.

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PREPARATION AND PROPERTIES OF PHOTOCATALYTICALLY ACTIVE TiO₂-SiO₂ COATINGS

A. Kloužková^a, M. Baudys^{a,b}, J. Krýsa^a

^a Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6.

^b Technopark Kralupy, University of Chemistry and Technology Prague, Žižkova 7, 27801 Kralupy nad Vltavou

This work deals with preparation and photocatalytic properties of two composite systems based on TiO₂ and SiO₂. The first composite system employs SiO₂ as a non-degradable sol-gel inorganic binder. Photoactive TiO₂ particles (P25, Evonik) were added (at various weight mass) into the prepared sol containing tetraethyl orthosilicate (TEOS) in ethanol. The various photocatalyst amounts were chosen with aim to achieve good stability and sufficiently high photocatalytic activity. Prepared suspensions were applied on glass substrates by dip-coating and then thermally treated at 300°C. The influence of the type of the glass substrate and the amount of TiO₂ in the applied suspension on the stability and photocatalytic properties was investigated. The second composite system consisted of two consequently deposited SiO₂ and TiO₂ layer. SiO₂ sol (TEOS in ethanol) was applied by sol-gel method (dip-coating technique) to a glass substrate to form a Na⁺ diffusion barrier layer. [1]. TiO₂ sol (titanium diisopropoxide bis (acetylacetonate), TAA) was then sprayed onto this SiO₂ layer by spray pyrolysis (SP) at 450°C [2]. The influence of the barrier layer, type of substrate, thickness of TiO₂ and subsequent calcination on photocatalytic activity was investigated.

Method, used for the determination of photocatalytic activity according to ISO standard [3], is based on the irreversible colour change of dye in ink which occurs on irradiated photocatalytic surface. The principle is the reduction of Resazurin dye to Resorufin, which is associated with colour change from blue to pink. In the case of the first composite system, the increase of TiO₂ content from 6 to 8%, results in almost 4 times higher photoactivity. In the case of the second composite system, presence of SiO₂ barrier layer and subsequent calcination of TiO₂ layers deposited by SP are essential to achieve photoactive coating. The most promising coating was selected, deposited on glass substrates and exposed to an accelerated weathering test in the QUV panel.

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Mo-BiVO₄ PHOTOANODES MODIFIED BY Co-Pi FOR PHOTOELECTROCHEMICAL APPLICATION

Š. Paušová^a, M. Neumann-Spallart^a, J. Krýsa^a

^a Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6.

Bismuth vanadate is a bright yellow compound used as a pigment since the 1980s. Moreover, BiVO₄ is becoming increasingly important as a visible-light-driven photocatalyst for photoelectrochemical (PEC) applications such as light assisted water electrolysis (oxidation of water to oxygen) or decomposition of organic pollutants where BiVO₄ can be used as a photoanode. Bismuth vanadate can be found in three different crystalline modifications: monoclinic, orthorhombic and tetragonal. The most suitable modification for light assisted water electrolysis is monoclinic BiVO₄ since its band gap energy is ~2.4 eV, tetragonal BiVO₄ should be avoided since it has ~3.0 eV band gap energy. However, low band gap BiVO₄ exhibits low efficiency due to poor electron transport, slow water oxidation kinetics, and low carrier mobility [1, 2]. Mo or W doping and/or surface modification with a water-oxidation co-catalyst can improve the electron conductivity and water oxidation kinetics [3, 4].

This work describes the preparation of Mo modified BiVO₄ thin film electrodes for light assisted water electrolysis from aqueous precursors using aerosol pyrolysis (AP) as a deposition method which does not require subsequent annealing. Mo-BiVO₄ was also further modified by surface deposition of cobalt phosphate (Co-Pi) co-catalyst.

The modification by Mo significantly increased the value of photocurrent (obtained values were more than 10-times higher than for pure BiVO₄), the highest increase was observed for BiVO₄ containing 14 mol% of Mo [5]. These layers were then used for Co-Pi modification. Co-Pi modification was performed by photodeposition under solar simulator irradiation (intensity 1 sun) from a solution containing phosphate buffer (pH 7) and cobalt chloride. Co-Pi deposition onto the photoanode surface yielded cathodic shifts of the onset potentials for water oxidation. The deposition time of the Co-Pi layer plays an important role in photoanode performance, the obtained photocurrent values were 2-4-times higher than for AP deposited BiVO₄ layers depending on the time of Co-Pi deposition (10, 20, 30, 40 min). The highest increase of photocurrent density was observed for 30 min deposition.

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Fe₂O₃ BASED SEMICONDUCTOR PHOTOANODES FOR LIGHT ASSISTED WATER ELECTROLYSIS

T. Imrich, M. Neumann-Spallart, J. Krýsa

Department of Inorganic Technology, University of Chemistry and Technology Prague,
Technická 5, 16628 Praha 6, Czech Republic

As an energy carrier, hydrogen has been extensively studied to satisfy the increasing demand on green energy. Efficient production of hydrogen from water under sunlight is one of the challenging and important topics in hydrogen energy technology where nanostructured materials represent a significant role. Nanomaterials are used for the preparation of photoanodes and photocathodes. Photoanodes are based on n-type semiconductors, especially (Ti, W, Fe) [1]. This work was focused on the preparation and characterization α -Fe₂O₃ (hematite) layers.

Hematite photoanodes were prepared by aerosol pyrolysis (AP) on transparent substrates (fluorine doped tin oxide (FTO) on glass) with the aim of obtaining high photocurrents and incident photon to electron conversion efficiency (IPCE). Films of TiO₂ (titania) were deposited on the top of hematite layers by dip coating and spray pyrolysis in order to increase stability in acidic media and reduce the extent of photocorrosion [2,3]. The structural, morphological and optical properties of the deposited films were determined by X-ray diffraction, field emission scanning electron microscopy (FE-SEM) and UV-vis absorption spectroscopy. Photoelectrochemical measurements were performed by voltammetry and amperometry.

Photocorrosion competes with water oxidation by valence band holes. The extent of photocorrosion in 1 M H₂SO₄ was tested after passing a certain amount of charge through the system (illumination time 6 h, applied potential 1.55 V vs. Ag/AgCl) followed by elemental analysis of the electrolyte (iron content) by ICP (inductively coupled plasma spectrometry). Corrosion of hematite in acid, in absence of light, was found negligible for the time period of the photoelectrochemical experiments. The Faradaic efficiency of the photocorrosion reaction in 1 M sulphuric acid was 0.47% for an unprotected hematite electrode, decreasing to 0.17%, but on the expense of photocurrent (decrease of up to 40 %), for a hematite electrode covered with a layer of TiO₂ coated by spray pyrolysis, thus proving the beneficial role of TiO₂ in protecting hematite against photocorrosion [3,4].

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^a Department of Chemistry and Physics of Materials, University of Salzburg, Jakob-Haringerstr. 2a, 5020 Salzburg

Biological photosynthesis as a life maintaining process on earth is based on the conversion of solar energy into chemical energy [1]. The same principle of energy conversion is used in photocatalysis and photoelectrochemistry for the generation of solar fuels. In these processes, the reduction of water or CO₂ results in the generation of storable H₂, CO and hydrocarbon fuels. Consequently, photocatalytic and photoelectrochemical processes are relevant in today's renewable energy research. [2] However, efficiency and long-term stability need to be improved for practical implementation [3].

Suitable electrode materials for photocatalytic applications should exhibit properties such as long charge carrier lifetimes, suitable band edge positions versus the hydrogen and oxygen evolution reaction and stability in aqueous media [4]. Oxynitrides show bandgaps in the range of the visible light energy and harvest therefore sunlight more efficiently than the related oxides, which absorb in the ultraviolet [5]. LaTiO₂N (LTON) as a perovskite-type oxynitride with a bandgap of 2.1-2.2 eV has proven to be a suitable material for the fabrication of photoanodes in the photoelectrochemical water-splitting process. [4, 6]

LTON particles are prepared by nitridation of the oxide precursor La₂Ti₂O₇ that is prior synthesized by scalable solid-state chemical reactions. Particle based LTON photoanodes are consequently fabricated by electrophoretic deposition. [4, 6, 7] The charge carrier transport efficiency can be notably improved by subsequent post-modification techniques such as dip-coating of the LTON electrode in Ti(OEt)₄ followed by annealing to create an a-TiO₂ network. [4] Moreover, improvements in efficiency and stability are achieved by adding co-catalyst and protection layers. [8] The scalable photoanodes are characterized by photocurrent measurements under AM 1.5G illumination, while the nanostructure of LTON particles and the microstructure of the electrodes are investigated by electron microscopic methods with the goal to relate material and electrode composition and architecture to photoelectrochemical performance.

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CATALYST COATED MEMBRANE - NEW APPROACH IN THE ALKALINE WATER ELECTROLYSIS PROCESS

M. Plevová^a, J. Hnáč^a, J. Žitka^b, M. Paidar^a, K. Bouzek^a

^a Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6, Czech Republic; e-mail: plevovam@vscht.cz

^b IMC CAS, Heyrovského nám. 2, 16206 Prague, Czech Republic

Water electrolysis together with fuel cells is currently one of the most studied electrochemical technologies. These technologies should be involved in a hydrogen economy, where excessive electrical energy from renewable sources is used to produce “green” hydrogen, which can be transformed back to electricity in a fuel cell. One of the industrially used technology of the water electrolysis is alkaline water electrolysis (AWE) whose main advantage over polymer electrolyte membrane (PEM) water electrolysis is the use of non-Pt metals as catalysts [1].

AWE is currently working with an inorganic diaphragm as a separator and concentrated liquid electrolyte is thus needed. But, it can be optimized using an anion selective polymer separator, which also allows us to prepare a membrane electrode assembly (MEA), where catalyst is applied either on to the substrate, referred to as a catalyst coated electrode (CCE) or on to the membrane, referred to as a catalyst coated membrane (CCM). CCM has several advantages over CCE. For example, there is a better contact between the catalyst and membrane and we can work with thinner layer [2]. The catalyst layer is composed of a catalyst powder and polymer binder. The binder is important for securing of the ionic contact and making the catalyst layer more compact. Because of these properties of the binder, ratio of catalyst:binder needs to be investigated. For CCE, typically 90:10 ratio is used [3], but for CCM this ratio needs to be modified.

In this work, we prepare and study CCMs with varying ratio of catalyst and binder. After evaluating the influence of the ratio, catalyst particle size will be further investigated. As an anion selective membrane block copolymer polystyrene-ethylene-butylene-styrene (PSEBS) with 1,4-diazabicyclo[2.2.2]octane (DABCO) functional groups is used. We use non-Pt catalyst, specifically NiCo₂O₄ as an anode catalyst and NiFe₂O₄ as a cathode catalyst. Performance of the AWE in the form of the load curves is measured. Electrochemical impedance spectroscopy (EIS) is used to evaluate the ohmic and polarization resistances of the system and SEM is used to observe the morphology of prepared CCMs. The obtained results show the possibility to achieve the high current densities with lower catalyst load. CCM thus represents a promising way of improving the alkaline water electrolysis technology.

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NiCoP_x CATALYST FOR ELECTROCHEMICAL WATER SPLITTING: ACTIVITY AND STABILITY UNDER THE ALKALINE WATER ELECTROLYSIS CONDITIONS

M. Ďurovič^a, J. Hnát^a, K. Bouzek^a

^a Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6.

Water electrolysis, in combination with renewable energy sources, has come to the forefront of interest during the last decade because of its ability to efficiently convert excess electrical energy into chemical energy of hydrogen. On an industrial scale, the most well-established route is that of alkaline water electrolysis (AWE). However, since this technology was originally designed for long-term stable operation, the above-mentioned combination with renewable energy sources places new demands on the process. Hence, in recent years significant research activity has focused on different aspects of AWE with the aim to increase its efficiency and flexibility. One of the important, and thus most widely investigated, topics in this field is to find an inexpensive electrocatalyst with high stability in an alkaline environment and good catalytic activity for both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).

In this work, NiCoP_x catalyst was synthesized by cathodic electrodeposition on Ni substrate and tested under the AWE conditions. The composition, morphology along with the transformation of the material during the AWE process were characterized by several analytical methods - XRD, XPS, SEM, etc. The electrochemical properties were evaluated by means of Tafel analysis, cyclic voltammetry and electrochemical impedance spectroscopy. The results suggest excellent catalytic activity of the material for both OER and HER. The composition and morphology of the material changes under the oxidative conditions in alkaline media – formation of corresponding oxides and hydroxides. These species show enhanced catalytic activity for the OER but significantly lower activity for the HER.

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ELECTROCHEMICAL REMOVAL OF ORGANIC POLLUTANTS FROM PROCESS WATER

K. Denk^a, A. Giurg^a, M. Paidar^a

^a Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6.

Persistent organic pollutants, which can be found in process water from industrial or agricultural sources, are often difficult to remove by usual water treatment. Furthermore, the pollutants can be toxic for bacteria used in water treatment and they can stay in the environment [1,2].

Usual ways of dealing with persistent pollutants are: (i) physical methods (adsorption on activated carbon and subsequent burning) [3] or (ii) chemical procedures. The latter relate to oxidation caused by chemical agents, *i.e.* chlorine or potassium permanganate. Chemical procedures utilizing OH· radicals are more advanced in comparison with previously mentioned and are thus called advanced oxidation processes (AOP) [4]. The OH· radical has high standard reduction potential (2.8 V vs. SHE, in acidic conditions) and is capable of mineralizing even persistent pollutants [5].

Electrochemical AOP (EAOP) offer a highly flexible way of removing organic pollutants from waste-water by generating the OH· radical electrochemically. EAOPs usually do not require addition of other chemicals into the processed water but sometimes they require increase in conductivity or acidification. This is an advantage in comparison with *i.e.* treating water with chlorine because it can cause chlorination of organic components which is undesirable [6].

Using electrodes with high overpotential for oxygen evolution reaction resolves in two possibilities. With low current loads, organic pollutants are oxidized directly on the surface of the electrode by the adsorbed OH· radical. With high current loads, apart from direct oxidation, an oxidizing agent such as O₃ (ozone) or S₂O₈²⁻ (peroxydisulfate) is generated and reacts with the organic species in the bulk of the solution [7].

Boron doped diamond (BDD) electrode and activated titanium anodes (ATA) based on SnO₂ doped by Sb were utilized for removing a model pollutant (acid orange 7) and a real industrial liquid waste. Concentrations of the pollutants were evaluated by UV-Vis spectrophotometry.

BDD electrode showed excellent results in terms of organic pollutants removal and stability. ATA electrodes show good removal capabilities but suffer from deactivation with higher current densities.

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LIGHT INDUCED CHARGE SEPARATION AND COMPETITIVE DEACTIVATION PROCESSES IN METAL OXIDE NANOSTRUCTURES

T. Berger, N. Siedl, M. Niedermaier, T. Schwab, O. Diwald,

Department of Chemistry and Physics of Materials, Paris-Lodron Universität Salzburg, Jakob-Haringer-Strasse 2a, A-5020 Salzburg, Austria.

Design and engineering of photoactive materials for photocatalysis is a complex endeavor. This is because many mechanistic steps are intertwined, so that a definite assignment of determining factors underlying the materials' photoactivity is demanding.[1,2] Microstructural features as well as intrinsic and extrinsic defects related to the nanoparticles ensemble critically affect the branching ratio between the utilization of photogenerated charges and their detrimental loss via recombination. In our group we have developed spectroscopy-based methods to qualitatively and quantitatively assess photoexcitation and charge trapping processes in the volume or at the surface of semiconducting metal oxide nanostructures. These can directly react with adsorbed molecules and transform into surface radicals with sufficient reactivity to undergo subsequent reactions.[2]

In this presentation, we will show how the time-dependent evolution of paramagnetic trapped holes and electrons on ensembles of metal oxide nanocrystals (with particle numbers in the range between 10^{13} and 10^{14}) can be tracked by CW X-band EPR measurements. Slow charge trapping processes occurring on a time scale of minutes, related saturation levels and their temperature dependence reveal important quantitative and qualitative insights into the role of i) dopants and impurities on the photoactivity of the host oxide [3], ii) solid-solid interfaces and beneficial heterojunctions, and iii) the impact of adsorbates on photoactivity of the metal oxide nanoparticle ensemble.[2] In another example, we will demonstrate that the distribution over the different exciton annihilation channels in colloidal ZnO nanoparticles sensitively depends on interface composition and the intensity of the photoexcitation light. A complementary photoluminescence and EPR spectroscopy study revealed key factors determining the optoelectronic performance of colloidal ZnO nanocrystals.[4]

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FLOW-FIELD GEOMETRY AND ITS IMPACT ON THE PEM FUEL CELL PERFORMANCE

K. Bouzek, R. Kodým, M. Drakselová, M. Paidar

Department of Inorganic Technology, University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6.

Utilisation of methods of the mathematical modelling represents already for decades well established approach in an effective design and optimisation of chemical, including electrochemical, technologies. Electrochemical engineering has used these methods primarily to solve problems related to the distribution of local values of the electrode potential and current densities. With rapid development of hardware, methods of numerical mathematics and related software, the numerical simulation approach has penetrated to a broad range of aspects of electrochemical technology design, including flow dynamics, so called CFD. In the present contribution an example of CFD methods application to the problem of the reactants flow distribution will be presented for an example of the PEM type fuel cell system. A comparison of different arrangements of the flow field channels geometry and their impact on the performance of the fuel cell stack has been selected for this purpose. This problem will be studied in a various scales in order to document impact of selected parameters and approaches on the simulation of this complex problem.

In order to solve this problem, at first simplified flow channels geometry have been manufactured and used to determine a pressure drop associated with gas flow under typical fuel cell operating conditions. Results have been used to validate the CFD mathematical model developed. In the next step permeability of the porous phase, i.e. gas diffusion layer was determined for both primary directions (through- and in-plane). It was followed by simulation of industrial scale flow fields of selected geometries documenting their specific properties. In the last step, the data and modelling approaches developed have been applied to simulate flow distribution in an operating industrial scale fuel cell stack. Macrohomogeneous approach developed previously [1] was used to accomplish this task.

The results obtained clearly document importance of the flow-field geometry, especially on the cathode side of the cell. Significant local oxidant starvation was observed under certain conditions. Surprisingly, although the cell life-time was significantly impacted by this effect, stack global load curve did not indicate any potential issue. This fact further stresses importance of mathematical modelling as an efficient tool to obtain local information on the distribution of the quantities in the studied unit, almost independently of its size and complexity.

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