



Turku University Centre for Materials and Surfaces
(www.utu.fi/matsurf)

13th ANNUAL MATSURF SEMINAR



DEPARTMENT OF PHYSICS AND ASTRONOMY
QUANTUM AUDITORIUM
NOVEMBER 04, 2019



Turun yliopisto
University of Turku



10.30 **Opening of the seminar:** NN

10.35 Ermei Mäkilä and Dr. Sari Granroth (Industrial Physics + Materials Research Labs)

New research infrastructure for surface and materials characterization at the Department of Physics and Astronomy

11.00 Sergio E. Domínguez (Lab of Materials Chemistry and Chemical Analysis)

Studies on cationic polythiophenes with hydrogen-bonding donor capabilities

11.20 **Invited lecture:** Prof. Laeticia Petit (Tampere University)

Glass development to improve the performance of the material

12.10 Lunch break

13.20 Dr. Muhammad Yasir (Materials Research Lab)

Segregation and surface diffusion of Al in FeAlCr alloy

13.40 Mukarram Khan (Wihuri Physical Lab)

Enhanced flux pinning isotropy by tuned nanosized defect network in superconducting $YBa_2Cu_3O_{6+x}$ films

14.00 **Invited lecture:** Dr. Ville Saarimaa (Top Analytica Oy Ab, Turku)

Nanorange X-ray analysis

14.50 Oral poster presentation (max 2 minutes one slide / poster)

15.10 Poster session (open end with snacks and drinks).



Ville Saarimaa, Top Analytica

ville.saarimaa@topanalytica.com



Synopsis

Surface analysis expert with broad "hands-on" material characterization experience with SEM/EDS & WSD, ToF-SIMS, ESCA, CA, XRF, FTIR, Raman, (S)TEM and AES. Familiar with process flows and material challenges from pulp & paper industry and colour coated steel industry.

Linkedin account: <https://www.linkedin.com/in/ville-saarimaa-b0465b6/>

University Education

Ph.D. (Chem. Eng.)

Åbo Akademi University 2007

Employment

CEO, project manager

Top Analytica Oy 2019-

Project manager

Top Analytica Oy 2009-2019

Research chemist

Ciba Finland Oy/BASF 2008-2009

Recent publications

"Synthesis of ZnO nanowires with supercritical carbon dioxide and post heat treatment", Kaleva, A., Nikkanen, J.-P., Heinonen, S., Saarimaa, V., Vuorinen, T., Hyvärinen, L., Levänen, E., *Nanotechnology*, 29(44):1-7 (2018).

"Tailoring of versatile surface morphologies on hot dip galvanized steel in wet CO₂: Aspects on formation, barrier properties and utilization as a substrate for coatings", Saarimaa, V., Kaleva, A., Nikkanen, J.-P., Manni, J., Lange, C., Paunikallio, T., Laihinen, T., Heinonen, S., Levänen, E., Väisänen, P., Markkula, A., *ACS Applied Materials and Interfaces*, 10(25):21730-21739 (2018).

"Convenient extraction method for quantification of thin zinc patina layers", Saarimaa, V., Kaleva, A., Paunikallio, T., Nikkanen, J.-P., Saara Heinonen, S., Levänen, E., Väisänen, P., Markkula, A., (2018), *Surf. Interface Anal.*, 50(5):564-570 (2018).



Prof. Laetitia Petit

Laetitia Petit received her Ph.D in Materials Science from the University of Bordeaux in France in 2002. She is currently an Associate Professor in the Photonics Laboratory at Tampere University (TAU, Finland). She is also an Adjunct Professor in the Faculty of Biomedical Sciences and Engineering at TAU and in the Inorganic Chemistry Laboratory at Åbo Akademi University (Finland). Her current research interests include the processing and characterization of novel active glasses/glass-ceramics and fibers for photonic applications. She focuses her research on understanding composition-structure-property relationship in these materials, with the goal to tailor new compositions to suit specific applications in photonics. Dr. Petit is co-author of 2 patents and more than 130 refereed publications, reviews, proceedings and book chapters and she has presented more than 20 invited presentations in her career.

New research infrastructure for surface and materials characterization at the Department of Physics and Astronomy

Ermei Mäkilä and Sari Granroth

Department of Physics and Astronomy, University of Turku

Recent infrastructure funding provided by the University of Turku has resulted in the acquisition of a new ultra-high resolution Field-emission Scanning Electron Microscope (FE-SEM) and a multi-technique X-ray Photoelectron Spectrometer (XPS).

The new FE-SEM has been installed in the P-floor of Quantum in the spring of 2019. The configuration of the microscope is designed to serve scientists from different fields, providing a wide range of conditions and analytical capabilities for samples which need high-resolution imaging such as low vacuum operation, STEM and cathodoluminescence detectors as well as an EDX spectrometer.

The acquisition process of the XPS was concluded in October 2019, with the instrument delivery and installation expected to take place in early 2020. The XPS will be installed also in Quantum, replacing the current spectrometer. Similarly as with the SEM, the configuration of the XPS is aimed to provide broad analytical options to characterize the surface structures of different samples with a high throughput.

In this talk we will discuss the capabilities and features of these instruments and how to gain access to them.

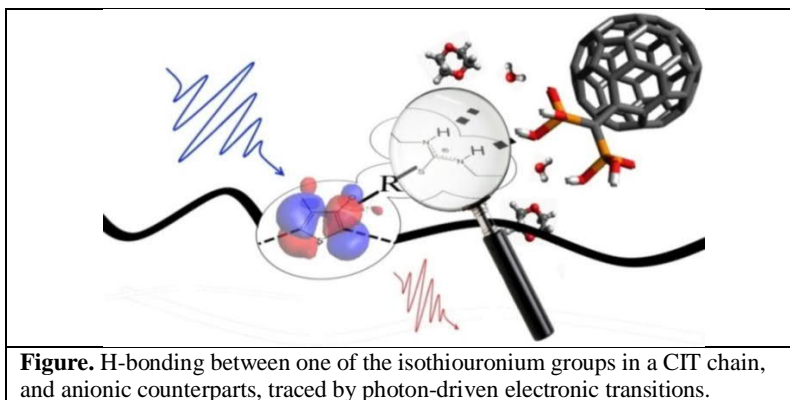
Studies on cationic polythiophenes with hydrogen-bonding donor capabilities

Sergio E. Domínguez, Pia Damlin and Carita Kvarnström

Department of Chemistry, University of Turku, Turku University Centre for Materials and Surfaces (MATSURF), 20014 Turku, Finland
suesdo@utu.fi

This project focuses on cationic isothiuronium polythiophenes (CITs), a particular type of conjugated polyelectrolytes (CPEs). In general, CPEs combine a pi-conjugated polymer backbone with pendant ionic groups (cationic and/or anionic), which gives them chromo- and fluoro-phoric properties, and also solubility in water and other polar solvents. This structure provides CPEs with interacting driving forces (either with solvents or with other dissolved molecules) of conjugated polymers (pi-pi stacking and hydrophobic interactions) and of polyelectrolytes, such as coordination through electrostatic forces and hydrogen bonding (H-bonding). Polythiophene-CPEs in particular, have a high sensitivity to different stimuli, such as solvent (solvatochromism) or other chemical species (affinity chromism), which can be traced by fluorescence. Besides these properties, the isothiuronium cationic functionality in the CITs under study, gives them enhanced hydrogen-bonding (H-bonding) donor capabilities.

The properties in the CITs were utilized for studying how structure influences on functions such as (i) electronic properties (ionization potential, electron affinity, optical transitions) and (ii) polymer-solvent, polymer-polymer, polymer-quencher and polymer-solid substrate interactions, by varying systematically the polarity/H-bonding capacity of the solvent. The optical properties of the CITs were traced by steady-state absorption-fluorescence spectroscopic techniques in order to track molecular changes, while their aggregation was studied by electron paramagnetic resonance (EPR) spectroscopy, using paramagnetic probes with different ionic and hydrophobic constituents. Cyclic voltammetry, DLS and computational chemistry methods were used in order to obtain complementary information.[1-5]



REFERENCES

- [1] Damlin, P. et al. "Study of the electrochemical and optical properties of fullerene and methano[60]-fullerenediphosphonate derivatives in solution and as self-assembled structures", *RSC Advances* **2014**, 4, 8391-8401.
- [2] Domínguez, S. E. et al. "Effect of alkoxy-spacer length and solvent on diluted solutions of cationic isothiuronium polythiophenes", *RSC Advances* **2017**, 7, 7648-7657.
- [3] Domínguez, S. E. et al. "Effect of Spacer Length and Solvent on the Concentration-Driven Aggregation of Cationic Hydrogen-Bonding Donor Polythiophenes", *Langmuir* **2018**, 34, 7364-7378.
- [4] Domínguez, S. E. et al. "Hydrogen-bonding mediated interactions between a water-soluble polythiophene-fullerene pair with two-point hydrogen-bonding capabilities, as a function of fullerene concentration and polarity and hydrogen-bonding capacity of the solvent". *Submitted*
- [5] Domínguez, S. E. et al. "Cationic imidazolium polythiophenes: effects of imidazolium-methylation on solution concentration-driven aggregation and surface free energy of films processed from solvents with different polarity". *Submitted*

Glass development to improve the performance of the material

L. Petit

Photonics Laboratory, Tampere University, FI-33101 Tampere, Finland

Email: Laeticia.petit@tuni.fi

The fabrication of new rare-earth (RE) doped glasses has attracted lots of research interests, the improvement in the performances of the glasses remaining the prime objective of the studies. Silica glass, as a host material, has proven to be very attractive because of its wide wavelength range with good optical transparency and high mechanical strength, just to cite few attractive properties. However, RE tend to cluster in silica glasses. Therefore, phosphate glasses have been of great interest as they are good host materials due to their ability to incorporate high amount of RE.

Because the local environment around the RE is of paramount importance for determining the optical properties, there is a constant interest in investigating new RE doped glasses with improved spectroscopic properties. A route of interest to improve the spectroscopic properties consists of controlling the RE optical response independently of the glass composition when developing new optical materials. Different techniques have been developed: one technique consists of precipitating RE doped nanoparticles directly in-situ in the glass. These glass-ceramics (GCs) are usually prepared by conventional melting followed by a thermal treatment of the glass. The GCs can exhibit significantly enhanced optical properties (such as absorption and emission cross-section and energy transfer rates) compared to their glassy counterparts, if the crystalline phase of the desired nature and structure precipitates around the rare-earth ions. Indeed, due to the crystalline environment surrounding the RE ions, the RE-doped glass-ceramics combine glass properties (large flexibility of composition and geometry) with some advantages of the RE-doped single crystals (higher absorption, emission and lifetimes). However, the heat treatment does not necessarily lead to the bulk precipitation of rare-earth doped crystals. Therefore, a new route was developed in order to prepare glasses, which contain rare-earth doped crystals. In this technique, the crystals doped with RE are first synthesized and then added in the glass batch after the melting. The main challenge with this novel route of preparing glasses is to balance the survival and dispersion of the particles in the glasses.

In this presentation, we will review our work on the development of new phosphate glasses, glass-ceramics and glasses which contain particles. First, we explain how these materials are prepared and characterized. We discuss the challenges related to the preparation of the glasses, which contain crystals. We will show that some of the promising glasses can be drawn into biophotonic fiber in the prospect of developing an innovative biosensor. Finally, we will show that irradiation can also be used to enhance the spectroscopic properties of glasses.

Segregation and surface diffusion of Al in FeAlCr alloy

S. Granroth, M. Yasir, M. Heinonen, R. Perälä, A. Pavlov, T. Kilpi, H. Sinkkonen, E. Kukk, and K. Kokko

Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland

I. MacLaren, and S. Andersson

University of Glasgow

Fe-Al alloys due to their remarkable resistance to corrosion and high strength are very important for high performance construction and engineering materials for numerous commercial applications like home cutlery, industrial equipment, surgical instruments, automobiles or nuclear reactors. The good corrosion resistance of Fe-Al alloys in oxidizing environment at high temperatures is obtained due to the formation of highly stable and self-healing Al oxide protecting layer at the sample surface. The addition of Cr in the alloy is known very beneficial to the alloy property. The Cr inclusion in the alloy boosts the desired sweeping of Al content from the bulk of the alloy and resulting the advantageous high concentration of Al at surface without compromising the alloy properties. Despite the numerous FeCrAl studies, the mechanism behind formation of stable oxide at the alloy surface is still not very well understood.

The aim of the study is to investigate the reaction occurring during the initial stages of oxidation process and the role of Cr concentration in the Al surface segregation in the Fe-Cr alloys that can lead to design a fabrication process to grow protective oxide scale. For that purpose, we examine oxide growth on FeCrAl alloy samples at high vacuum system. In addition to that, the effect of both the Cr concentration as well as the variation in temperature on Al surface segregation is also studied.

Enhanced flux pinning isotropy by tuned nanosized defect network in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ films

Mukarram Zaman Khan^{1,2,*}, Elmeri Rivasto^{1,2}, Jussi Tikkanen¹, Hannes Rijckaert³, Mika Malmivirta¹, Maciej Oskar Liedke⁴, Maik Butterling⁴, Andreas Wagner⁴, Hannu Huhtinen¹, Isabel Van Driessche³, and Petriina Paturi¹

¹Wihuri Physical Laboratory, Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland

²University of Turku Graduate School (UTUGS), University of Turku, FI-20014 Turku, Finland

³SCRiPTS, Department of Chemistry, Ghent University, Krijgslaan 281 S3, 9000 Ghent, Belgium

⁴Institute of Radiation Physics, Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany

*mukarram.z.khan@utu.fi

Abstract

Striving to improve the critical current density J_c of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (YBCO) thin films via enhanced vortex pinning, the interplay between film growth mechanisms and the formation of nanosized defects, both natural and artificial, is systematically studied in undoped and BaZrO_3 (BZO)-doped YBCO thin films. The films were grown via pulsed laser deposition (PLD), varying the crystal grain size of the targets in addition to the dopant content. The microstructure of the PLD target has been observed to have a great impact on that of the deposited thin films, including the formation of vortex pinning centers, which has direct implications on the superconducting performance, especially on the isotropy of flux pinning properties. Based on experimentally measured angular dependencies of J_c , coupled with a molecular dynamics (MD) simulation of flux pinning in the YBCO films, we present a quantitative model of how the splay and fragmentation of BZO nanorods artificially introduced into the YBCO film matrix explain the majority of the observed critical current anisotropy.



13th Annual MatSurf Seminar 04.11.2019

Nanorange X-ray analysis

Ville Saarimaa, Top Analytica

Abstract

Energy dispersive x-ray spectroscopy (EDS), combined with scanning electron microscopy, has been the state-of-the-art element analysis tool for material scientists for decades. EDS systems are efficient in materials characterization and quantitation of elements, but the conventional EDS systems do not allow measurement of thin layers, electron beam sensitive materials or specimens with low x-ray yield due to the detector configuration. Recently, a new detector type was launched with suitability for improved lateral resolution and surface sensitivity, and possibility to analyze beam-sensitive materials at very low ion beam currents. In this presentation, results from measurement of a wide range of different samples are discussed with an emphasis to highlight the benefits of the detector for various materials.

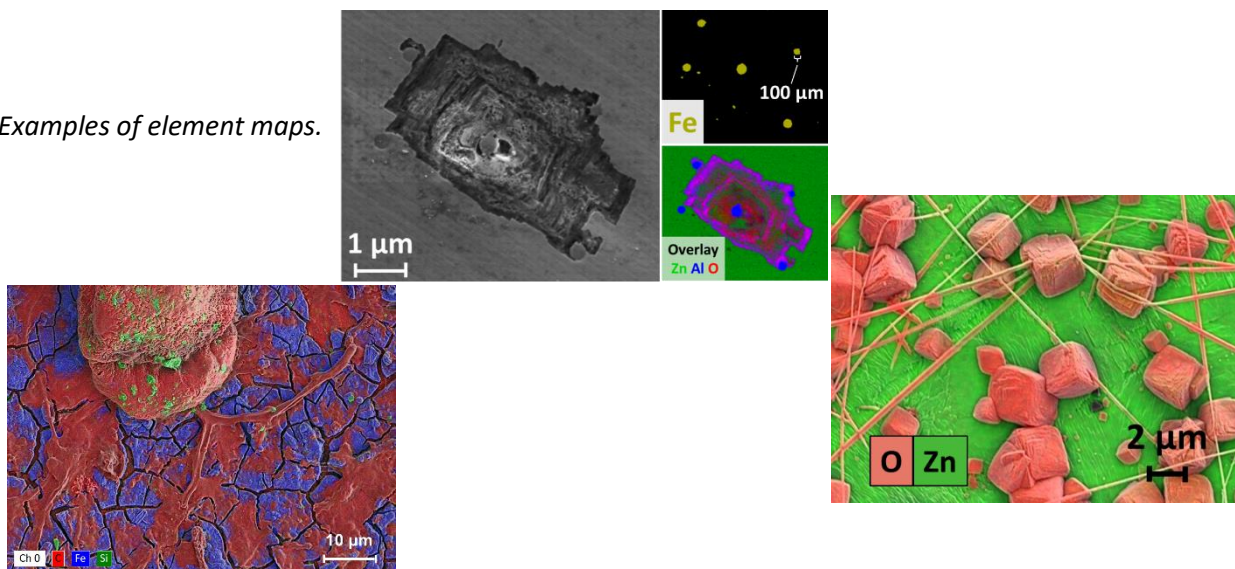


FlatQUAD detector with four chips for separate signal processing. Primary electron beam passes through the center hole. Image : www.bruker.com.

Methods

Scanning electron microscopy (SEM) imaging was performed using a Zeiss Gemini 450 instrument, and the element composition mapping was performed using a Bruker QUANTAX FlatQUAD energy dispersive x-ray spectroscopy system. Cross sections for SEM characterization were prepared using an Ilion+ Advantage Precision Cross-section System (Model 693, Gatan).

Examples of element maps.



POSTERS (presenting author in alphabetical order)

1) Hannah Byron

A rapid, zeolite-free synthesis of the optically versatile mineral hackmanite

2) Lokesh Kesavan

Electro-catalytic Reduction of CO₂ Using Supported Au, Pd Nanoparticles

3) Sachin Kochrekar

Spectroscopic and theoretical investigation of keto functionalized porphyrin polymers

4) Adefunke Koyejo

Electrocatalytic evaluation of biobased reduced graphene oxide supported on Au nanoparticles for carbon dioxide reduction

5) Antti Lahti

In search of the ground-state structure of SiO₂

6) Zahra J. Rad

Modification of chemical Si-surface cleaning with vacuum treatment

7) Elmeri Rivasto

Growth of the nanorods within YBCO films deposited on an advanced IBAD-MgO template

A rapid, zeolite-free synthesis of the optically versatile mineral hackmanite

Hannah Byron^{1*}, Isabella Norrbo¹ and Mika Lastusaari^{1,2}

¹ Department of Chemistry, University of Turku, Turku, Finland

² Turku University Center for Materials and Surfaces (MatSurf), Turku, Finland

*hcbyro@utu.fi

The naturally occurring mineral hackmanite ($\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Cl},\text{S})_2$) is known for its optical properties, which include photoluminescence, persistent luminescence and photochromism.¹ These properties give it potential for many industrial applications, and synthetic hackmanites can be produced using a range of methods and starting materials. The most rapid of these to date was developed by Carvalho *et al.* using a microwave-assisted structure conversion (MASC) to produce hackmanite from zeolite A (NaAlSiO_4).² It is also possible to synthesise hackmanite from simpler starting materials, by reacting stoichiometric amounts of Al_2O_3 , SiO_2 , NaCl , Na_2SO_4 and a source of Na_2O (e.g. Na_2CO_3), via a solid-state or hydrothermal method.³ In this research, these two ideas have been combined to produce hackmanite with multiple optical properties from simple oxide starting materials heated together in a microwave.

Three samples are explored in this work, each produced under different microwave conditions and then reduced for 2h at 850 °C under an N_2/H_2 atmosphere. Analysis of the crystal structure by powder x-ray diffraction (pXRD) revealed all the products showed the characteristic peaks of a sodalite structure. The growth of this structure after each cycle of microwave heating can be seen for sample **M2** (Fig 1). Scherrer analysis of the peak at ca. 24.3 ° revealed that all the samples contained domains around 100nm in size, likely due to the rapid synthesis times. The only identifiable impurity in these samples was unreacted NaCl, easily removed through washing.

These materials were also observed to have the expected white photoluminescence of hackmanite and **M1** showed a very weak persistent luminescence. Photochromism was not visible to the naked eye, however a change in reflectance corresponding to a slightly purple colouration was detected for sample **M1** by a spectrometer.

These observations lead to the conclusion that hackmanite was made successfully using this method. The weakness of the optical properties, particularly the afterglow, is thought to be because these materials had small domain sizes. However, if improvements were made to the synthesis it could become possible to produce low-cost and tuneable hackmanites using this rapid low-energy method. Further investigation into optimisation of the synthesis method and possible dopants to improve optical properties could be carried out in the future.

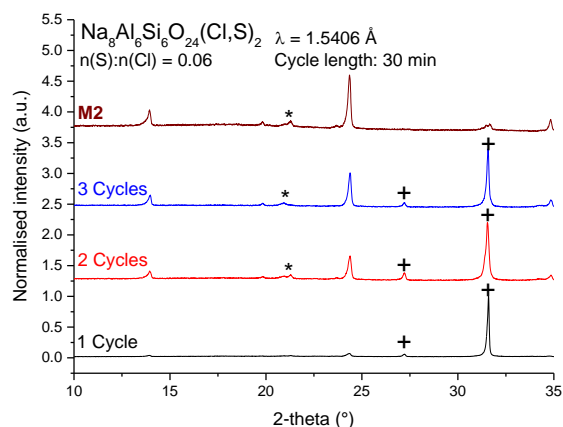


Figure 1: XRD patterns of **M2** showing the growth in peaks corresponding to the sodalite structure after each cycle of heating and compared to the final reduced product.

References

1. I. Norrbo, P. Gluchowski, P. Paturi, J. Sinkkonen and M. Lastusaari, *Inorg. Chem.*, 2015, **54**, 7717–7724.
2. J. M. Carvalho, I. Norrbo, R. A. Ando, H. F. Brito, M. C. A. Fantini and M. Lastusaari, *Chem. Commun.*, 2018, **54**, 7326–7329.
3. D. B. Medved, *Am. Mineral.*, 1954, **39**, 615–629.

Electro-catalytic Reduction of CO₂ Using Supported Au, Pd Nanoparticles

Lokesh Kesavan, Adefunke Koyejo, Pia Damlin, Carita Kvarnström*

University of Turku, Turku University Centre for Materials and Surfaces (MatSurf),
Laboratory of Materials Chemistry and Chemical Analysis,
Vatselankatu 2, FI-20014, Turku, Finland

Carbon dioxide, the potential industrial & anthropogenic waste, is a fast upcoming feedstock for fuels, chemicals, polymers, and other value added materials. CO₂ can be converted into these products either via chemically or biologically. Electro-reduction is one among the many chemical methods to valorize CO₂ into useful products like CO, CH₃OH, HCOOH etc⁽¹⁻³⁾. Electro-reduction of CO₂ using single crystal catalysts have been widely studied by the academic fraternity. But they are still model catalysts and not ready for real world applications. Hence there is a serious need to develop real catalytic materials to mitigate CO₂ efficiently and selectively to desired products. In 'real' catalyst front, size & shape controlled metal nanoparticles prepared via colloidal methods are the promising upcoming catalytic materials for CO₂ electro-reduction.

With colloidal methods, the metal precursor (Mⁿ⁺) is electronically reduced to metallic state (M⁰) by galaxies of reducing agents and maintained in its nanoparticle size or specific geometrical shape by stabilizer polymers. These nanoparticles are further immobilized on stable solid supports, in order to have ideal heterogeneous catalysts, which are further fabricated on the working electrode surface. These modified working electrodes are used in an electrochemical cell saturated with reactant CO₂, to catalyze the electro-reduction of CO₂ when the working potential is applied. We at Department of Chemistry, University of Turku, working out on such a material and modified electrode as shown in Fig. 1. We believe that these Au, Pd nanoparticles can turn promising candidates for recycling CO₂ to chemicals/fuels, if they are developed diligently by keeping their size, geometrical shapes, surface exposed atoms in account. Thus, greenhouse gas like CO₂ can be made 'a threat no-longer'.

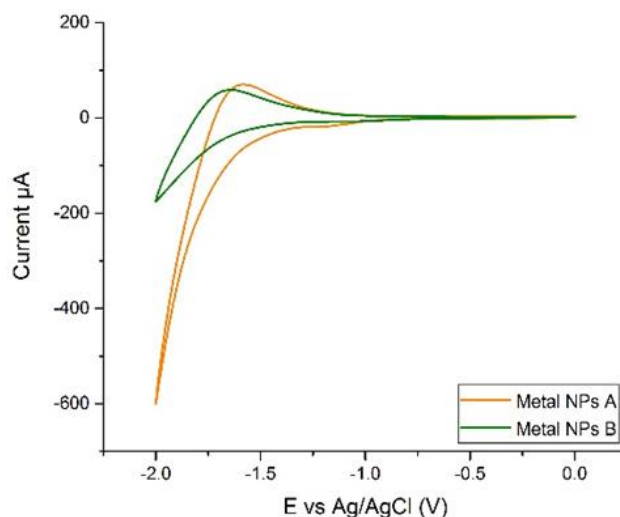


Figure 1: Electro-catalytic reduction of CO₂ using supported Au, Pd metal nanoparticles

References

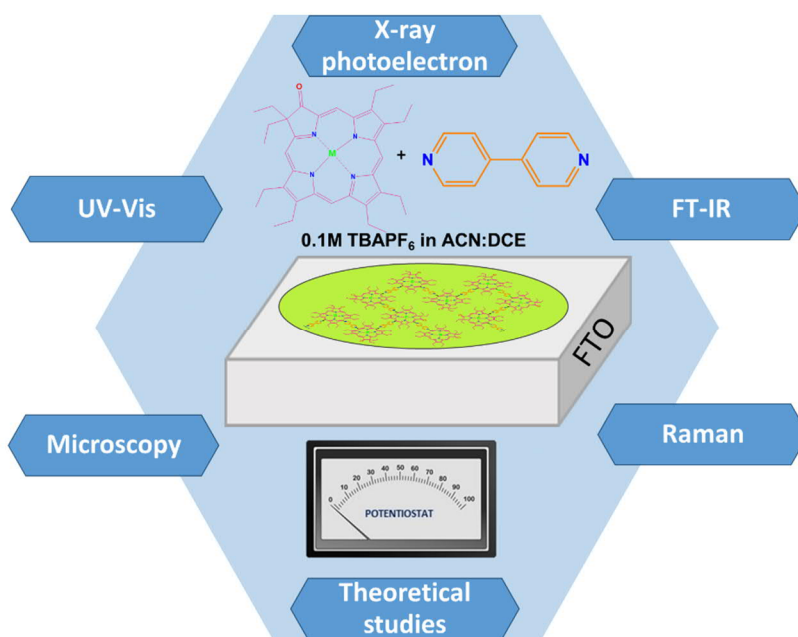
1. T. Yoshiyuki, N. Ikumi, M. Masayuki, *Electrocatalysis*, **2019**, 10 (1), 29-34
2. S. Luyu; L. Weixin; Z. Rui; et al., *International Journal of Electrochemical Science*, **2019**, 14 (1), 114-125
3. A. Chenguang; Y. Jiongliang; Z. Jiazhong, *Journal of the Electrochemical Society*, **2018**, 165 (16), H1066-H1071

Spectroscopic and theoretical investigation of keto functionalized porphyrin polymers

Sachin Kochrekar¹, Ajit Kalekar¹, Pia Damlin¹, Mikko Salomäki¹, Shweta Mehta², Kavita Joshi² and Carita Kvarnström¹

University of Turku, Department of Chemistry, Turku University Centre for Materials and Surfaces (MatSurf), Vatselankatu 2, FI-20014 Turku¹, Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Pune 411008 India².

Molecular catalyst based systems have always piqued interest due to their unique properties, consisting of a wide range of compounds containing transition metal complexes. Among these, catalyst based on M-N-C extended structures mostly metal porphyrins bears perceptible advantage of well-defined molecular structures, efficient and robust. That allows the functionalization and customization at atomic level to optimize and improve the overall catalytic performance and mechanistic study[1]. This work describes electropolymerization of functionalized macrocyclic metal complexes in presence of nucleophilic binders on the conductive surface and their detailed Spectroscopic analysis to understand their structure and properties. The interaction between the binder and the keto functionalized porphyrin was also evaluated by theoretical approach to fathom the polymerization process.



References:

1. Day, Nicholas U., Carl C. Wamser, and Michael G. Walter. "Porphyrin polymers and organic frameworks." *Polymer International* 64,7 (2015): 833-857.
2. Boudiaf, Moussa, et al. "Stable isoporphyrin copolymer: Electrochemical mechanism and behavior and photovoltaic properties." *Electrochimica Acta* 309 (2019): 432-449.

Electrocatalytic evaluation of biobased reduced graphene oxide supported on Au nanoparticles for carbon dioxide reduction

Adefunke Koyejo¹, Lokesh Kesavan¹, Pia Damlin¹, Minna Hakkarainen², Carita Kvarnström¹

¹Turku University Centre for Materials and Surfaces (MATSURF), Laboratory of Materials Chemistry and Chemical Analysis, University of Turku, Vatselankatu2, FIN-20014, Turku, Finland, ...

² Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, Teknikringen 58, 100 44 Stockholm, Sweden
e-mail: adkoye@utu.fi

Carbon dioxide (CO₂) has a bad reputation as a greenhouse gas responsible for warming the planet (global warming) and changing the climate in harmful ways. Due to the tide of industrialization and our over reliance on fossil fuels, CO₂ concentration keeps increasing. With its increasing amount, comes pollution and extreme weather conditions, which presently, has become a matter of global concern [1]. CO₂ emissions can be stabilized by reducing or recycling CO₂ into value-added products. Electrocatalytic reduction of CO₂ is an environmentally clean technology capable of converting CO₂ with high rate and selectivity to gas phase (CO and CH₄) and liquid phase products (HCOOH, CH₃OH) [2]. Here, we report a one-pot synthesis of Au nanoparticles supported on biobased reduced graphene oxide as electrocatalysts for CO₂ reduction. Our study focuses on the activity of these electrocatalysts in room temperature ionic liquids (RTILs) [Hmim][BF₄], and an organic system (TBAPF₆/ACN). Results show that the reduction of CO₂ takes place at a more negative potential in the organic medium (-1.77 V vs Ag/AgCl) than in RTILs (-1.4 V vs Ag/AgCl). Catalytic activity and incorporation were further studied using Raman and Fourier transform Infra-red (FTIR) spectroscopy.

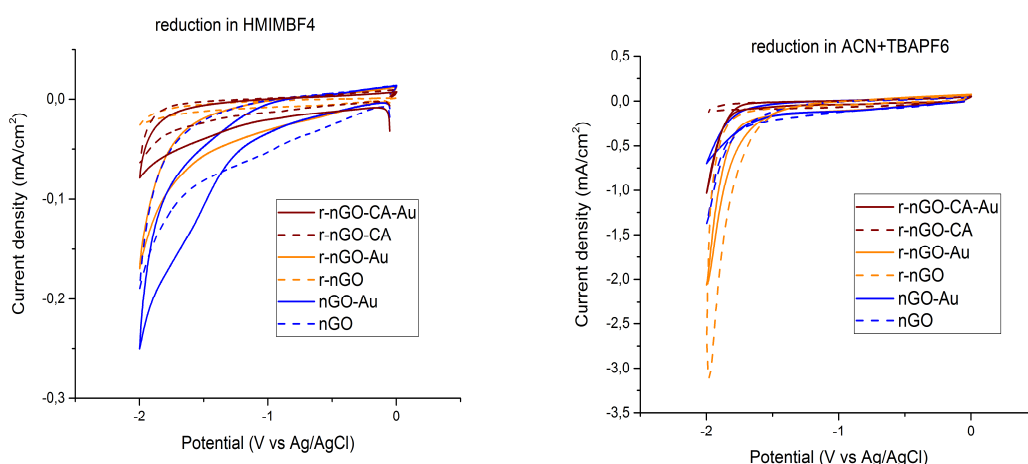


Fig 1: CO₂ reduction in (a) HMIMBF₄ and (b) TBAPF₆/ACN

In search of the ground-state structure of SiO₂

• **Antti Lahti**¹ **Ralf Östermark**² **Kalevi Kokko**¹

¹ *University of Turku, Department of Physics and Astronomy*

² *Åbo Akademi, Accounting Department*

Finding the ground-state structure of materials with large unit cells can be a challenging task. Especially with materials that have amorphous tendencies, like the silicon-dioxide we have chosen to study. This material has a known ordered ground state structure, but also exhibits a multitude of disordered low energy structures. We are trying to find this ordered ground state structure through different optimization methods using Genetic Hybrid Algorithm platform using semi-empirical potential for energy evaluation. The main focus has been in trying to guide the optimization search and analysing the found structures to understand how we can find the ground state structure among all the other local minima structures.

Here we present findings on the found structures and on few different approaches to this problem: mainly guiding the search through energy, bond count and order algorithm compared to a random "wandering" search. Energy turns out to be a very bad guide, while bond count and order give some promising results. They all share the same trait of that enforcing the guiding method will always not only lead to worse results but also increase the computational cost.

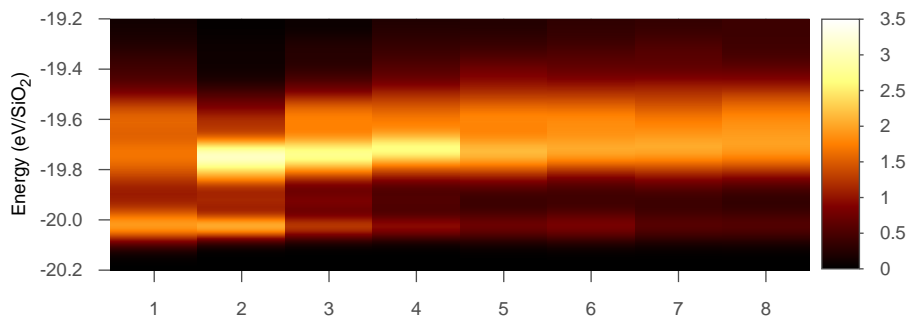


Figure 1: From left to right the intensity of energy guidance increases. Each vertical slice represents the distribution of found structures in energy. We see the focus of this distribution moves up in energy as we force the algorithm to adhere to energy guidance more strongly.

Modification of chemical Si-surface cleaning with vacuum treatment

J.-P. Lehtiö (1), Z. J. Rad (1), M. Yasir, J. Mäkelä (1), M. Kuzmin (1), E. Vuorinen (1), M. Punkkinen (1), P. Laukkanen (1), K. Kokko (1), R. Punkkinen (1), H.-P. Hedman (1), P. Repo (2), H. Savin (2)

(1) University of Turku, Finland, (2) Aalto University

This study tries to bridge between semiconductor industry and academic methods used to clean Si surface. In the industry, methods should be enough simple and scalable (for wafer size samples), while in academic methods, complicated equipment can be utilized and the size of the sample is small. This causes a difference between academic and industrial methods used for preparing Si surface (e.g. Refs.¹⁻⁵). In the industry, wet chemical treatments (RCA) are used to remove the native oxide and carbon contaminants from Si surfaces. These methods are simple and scalable, and a hydrogen or oxygen passivation layer is formed on the surface, but Si surface after this method is not well crystalline and this causes formation of defect levels in the interfaces between Si and metal/insulator layer. On the other hand, repeating ultrahigh vacuum flash heating (up to 1200 °C) for few seconds is utilized to clean surface of small Si samples (6×12 mm). This method provides a well crystalline and free of contaminants surface, but it is not scalable. This method cannot be utilized to clean wafer size samples, since it is a direct current heating, and in practice, it is done only on small samples.

In this work, a combination of wet chemical cleaning (industrial) and high vacuum heating at lower temperatures (600-800 °C) is used to clean the Si surface. Also, a controlled oxidation of cleaned Si surfaces was done in vacuum condition using previous results on crystalline oxidation of Si(100)⁶.

The validity of the cleaning method was tested by low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). Results showed that a crystalline Si surface is formed, and carbon and oxide contaminants are mostly removed in comparison to a reference sample, which was not cleaned.

To investigate the effects of controlled oxidation, HfO₂/Si(100)-based capacitors were prepared and measured by growing HfO₂ layer using atomic layer deposition (ALD) on cleaned and oxidized samples. The comparison of capacitance-voltage (C-V) curves reveals that the controlled pre-oxidation of Si enables to modify also fixed charge state at HfO₂/Si(100) junctions. Negative fixed charge of HfO₂ in the reference sample without the pre-oxidation causes the formation of hole inversion layer, which contributes to the inversion capacitance increase at high frequencies.⁷ The results indicate that the vacuum-based oxidation method opens way to adjust the fixed interface charge for controlling the threshold voltage and carrier blocking.

[1] P. Panchaipetch et al., IEEE J. Select. Top. Quant. Electr. 10, 89 (2004).

[2] B. J. O'Sullivan et al., J. Electrochem. Soc. 151 G493 (2004).

[3] P. D. Kirsch et al., IEDM (2006), DOI: 10.1109/IEDM.2006.346862.

[4] M. Kuzmin et al., Phys. Rev. B 90, 235405 (2014).

[5] H. Savin et al., Nat. Nanotechn. 10, 624 (2015).

[6] J.-P. Lehtiö et al., SISC (2017).

[7] É. O'Connor et al., J. Appl. Phys. 111, 124104 (2012).

Growth of the nanorods within YBCO films deposited on an advanced IBAD-MgO template

E. Rivasto^{1,2}, M. Z. Khan^{1,2}, Y. Zhao³, C. Chen⁴, J. Zhu⁴, J. Tikkanen¹, H. Palonen¹, H. Huhtinen¹ and P. Paturi¹

¹ Wihuri Physical Laboratory, Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland

² University of Turku Graduate School (UTUGS), FI-20014 Turku, Finland

³ Department of Electrical Engineering, Shanghai Jiao Tong University, 200240 Shanghai, People's Republic of China

⁴ Shanghai Superconductor Technology Co. Ltd., 200240 Shanghai, People's Republic of China

E-mail: elmeri.o.rivasto@utu.fi

Abstract. In order to enhance the flux pinning in high temperature superconductors for various applications, the growth of different diameter nanorods of BaHfO₃, BaZrO₃ and BaSnO₃ within the YBa₂Cu₃O_{6+x} matrix on advanced IBAD-MgO based template have been systematically investigated. Angular dependent critical current measurements and molecular dynamics simulations reveal differences in critical current isotropy between differently doped samples. Variation of nanorod diameter and their distribution enables more advanced optimization process of superconducting properties in wide temperature, field and angular range.

NOTES

NOTES



Turku University Centre for Materials and Surfaces (www.utu.fi/matsurf)

Participating laboratories:

- Laboratory of Materials Research (Prof. Kalevi Kokko, Prof. Edwin Kukk)**
- Laboratory of Industrial Physics (Prof. Jarno Salonen)**
- Wihuri Physical Laboratory (Prof. Kurt Gloos, Prof. Petriina Paturi)**
- Laboratory of Materials Chemistry and Chemical Analysis**
(Prof. Carita Kvarnström, Dr. Mika Lastusaari, Prof. Jukka Lukkari)
- Turku Clinical Biomaterials Centre – TCBC (DDS Lippo Lassila, Prof. Pekka Vallittu)**
- Laboratory of Electron Microscopy (Dr. Markus Peurla, Prof. emeritus Lauri Pelliniemi)**

Sponsors of this year's MatSurf Seminar:

- Department of Physics and Astronomy**
- Department of Chemistry**
- Top Analytica Oy Ab**