

Porous Materials @ Work for Sustainability

Summer School on Catalysis

**LP
03**

Leadproject initiative of
Graz University of Technology

**Summer School
2024**

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Program

	Monday, 8.7.	Tuesday, 9.7.	Wednesday, 10.7.	Thursday, 11.7.
09:00		Christoph Rameshan Heterogeneous catalysis	Dominik Eder Photocatalysis	Martin Sterrer Surface science model systems in heterogeneous catalysis
09:15				
09:30				
09:45	Registration			
10:00		Nina Grujicic	Lara Marie Novak	Nicolas Plumeré Electrobiotechnology for H ₂ production and CO ₂ reduction
10:15	Gregor Trimmel			
10:30	Welcome and introduction to catalysis	Coffee break	Coffee break	
10:45		Martin Krammer High temperature solid oxide electrolysis	Christophe Le Ret (Umicore) Catalysis - An industrial perspective	
11:00	Coffee break			
11:15				
11:30				Hrshikesh Joshi (Evonik) - Industrial zeolites
11:45	Christoph Winkler Tutorial - Basics of biocatalysis	Johann Hlina	Verena Lipic	
12:00				
12:15				Theodoros Dimopoulos Photoelectrochemical water splitting
12:30		Lunch break	Lunch break	
12:45				
13:00	Lunch break			
13:15				
13:30		Regina Kratzer Microbial carbon dioxide assimilation	Excursion	Closing
13:45				Lunch
14:00	Organisational			
14:15	Francesco Carraro	Christian Slugovc		
14:30	Porous biocomposites for biocatalysis and biosensing	Coffee break		
14:45				
15:00		Noelia Barrabes Nanocluster catalysis and operando XAFS		
15:15	Coffee break			
15:30				
15:45	Nikolaus Gorgas Cooperative effects between main group and transition metals	Christoph Winkler Photo-biocatalysis and organic synthesis		
16:00				
16:15	Get-together & poster session			
16:30				
16:45				
17:00				
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18:45				



Tutorial Talks



Porous biocomposites for biocatalysis and biosensing

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Proteins are a class of biomacromolecules that includes enzymes, antibodies and protein-based therapeutics. They can be exploited for different biotechnological applications, ranging from biocatalysis and biosensing to biomedicine. One of the main limitations to their widespread technological application are their fragility in hostile environments, their limited recyclability, and cumbersome products' purification. Thus, immobilization in porous solids is a strategy to enhance their stability and recyclability in biocatalysis and biosensing applications and to improve the efficiency of delivery in biomedicine. In this seminar, an overview about the research we are doing at Graz University of Technology on the immobilization of proteins into Metal Organic Frameworks (MOFs) and Hydrogen-bonded Organic Frameworks (HOFs) and the applications in the field of biocatalysis and biosensing of these innovative biocomposites will be discussed. In particular, the seminar will focus on i) Zeolitic Imidazolate Frameworks (ZIFs, a class of MOFs) biocomposites [1-3], ii) the recent development of HOFs biocomposites [4,5] and iii) the use of in situ techniques (e.g. Small and Wide Angle X-ray Scattering) to investigate the assembly of these porous frameworks around proteins [2,3,5].

References:

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- 2 Carraro F, Williams JD, Linares - Moreau M, Parise C, Liang W, Amenitsch H, Doonan C, Kappe CO, Falcaro P. *Angew. Chem.*, **2020**, 132 (21), 8200
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Cooperative effects between main group and transition metals: a new opportunity in catalysis?

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Bimetallic cooperation is an effect of great importance in catalysis. The synergistic interplay of two metal centres are common features in catalytic systems ranging from metalloenzymes in nature to the field of heterogeneous catalysis. On the other hand, organometallic transition metal complexes and their application in homogeneous catalysis have long been dominated by monometallic reactivity. In this contribution, the prospects of molecularly well-defined bimetallic systems in homogeneous catalysis and cooperative effects brought about by the close proximity of two metals will be highlighted. Emphasis will be given to systems combining transition metals with those of the main group series and to mechanisms by which bond activation occurs across these bimetallic structures. The synergisms and opportunities of bimetallic cooperation will be illustrated by recent studies on the reactivity of well-defined Iron-Aluminium complexes.



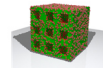
The role of heterogeneous catalysis in chemical energy conversion

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Heterogeneous catalysis plays a pivotal role in renewable chemistry including green fuels, offering a pathway to sustainable chemical processes. This form of catalysis involves solid catalysts facilitating reactions in different phases, typically gases or liquids, which allows for easy separation and reuse of catalysts, enhancing economic and environmental efficiency. Its importance in chemical energy conversion is underscored by its ability to drive reactions under milder conditions, reducing energy consumption and minimizing by-products. Heterogeneous catalysts enable the conversion of renewable feedstocks, such as biomass and CO₂, into valuable chemicals and fuels, thus supporting the transition from fossil-based to renewable resources. Moreover, they facilitate the development of green chemical processes by promoting higher selectivity and yield, reducing waste, and enhancing overall process sustainability. Through innovations in catalyst design and surface engineering, heterogeneous catalysis continues to expand its potential in achieving cleaner production methodologies, contributing significantly to the advancement in the e-fuels sector.

We show the crucial role of the reverse water-gas shift (RWGS) reaction for the development of sustainable aviation fuels (SAFs), offering a pathway to convert carbon dioxide (CO₂) into syngas (a mixture of hydrogen and carbon monoxide). This reaction is instrumental in utilizing CO₂ as a renewable carbon source for fuel synthesis. By efficiently converting CO₂ with hydrogen, preferably derived from renewable sources such as water electrolysis, the RWGS reaction generates syngas, which can be further processed via Fischer-Tropsch synthesis or other catalytic routes to produce high-quality aviation fuels. These fuels have the potential to significantly reduce the carbon footprint of the aviation industry, promoting a sustainable alternative to traditional fossil-based jet fuels. The RWGS reaction thus stands at the forefront of efforts to create a circular carbon economy, leveraging waste CO₂ and renewable hydrogen to produce sustainable aviation fuels, thereby contributing to both climate change mitigation and energy sustainability.



Material aspects of solid oxide electrolysis cells

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High temperature solid oxide electrolysis is a promising technology for energy storage as well as sector coupling purposes. Apart from being the electrolysis technology with the highest electrical efficiency it also offers fuel flexibility as it enables production of H_2 , CO or syngas. However, high operating temperatures lead to substantial requirements for the applied materials.

This contribution will deal with the applied materials for solid oxide electrolysis cells (SOECs) covering defect chemical considerations and the corresponding interplay with the prevailing chemical potential. Specifically, this will be exemplified in detail for mixed conducting perovskite oxides such as $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$ and their application as oxygen electrodes (anodes) in SOECs. Impedance spectroscopy on model thin film electrodes can be used to study these relations. Employing equivalent circuit models to fit these impedance spectra allows to obtain not only the surface oxygen exchange resistance but also the chemical capacitance.¹ From the latter important information about the defect chemistry of mixed conducting oxide electrodes can be obtained. Furthermore, degradation phenomena will be discussed with a focus on the oxygen electrode under SOEC operating conditions. Pore and crack formation in the electrolyte or at the oxygen electrode/electrolyte interface and even delamination of the oxygen electrode is often observed.^{2,3} Such degradation phenomena are caused by high internal gas pressures leading to mechanical stress. It is shown how such internal gas pressures can be detected and quantified using impedance spectroscopy and model calculations based on a real-gas equation (see Figure 1a).

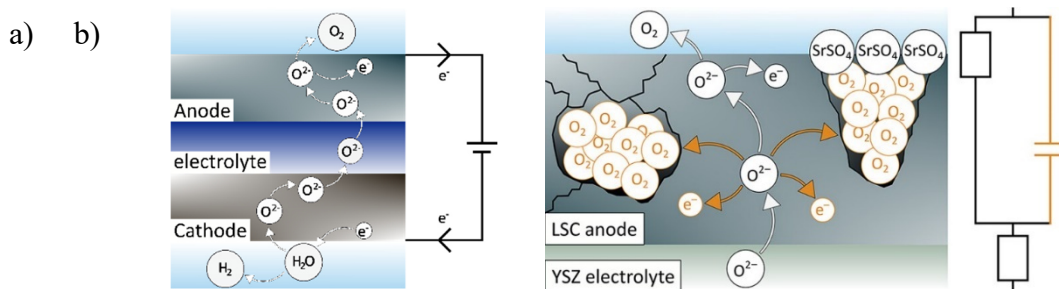
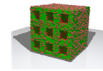


Figure 1. (a): Working principle of solid oxide electrolysis cells. (b): Sketch of the formation of high-pressure oxygen in pores of an oxygen electrode taken from Ref. [3].

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Hydrogen-oxidizing bacteria for microbial CO₂ assimilation

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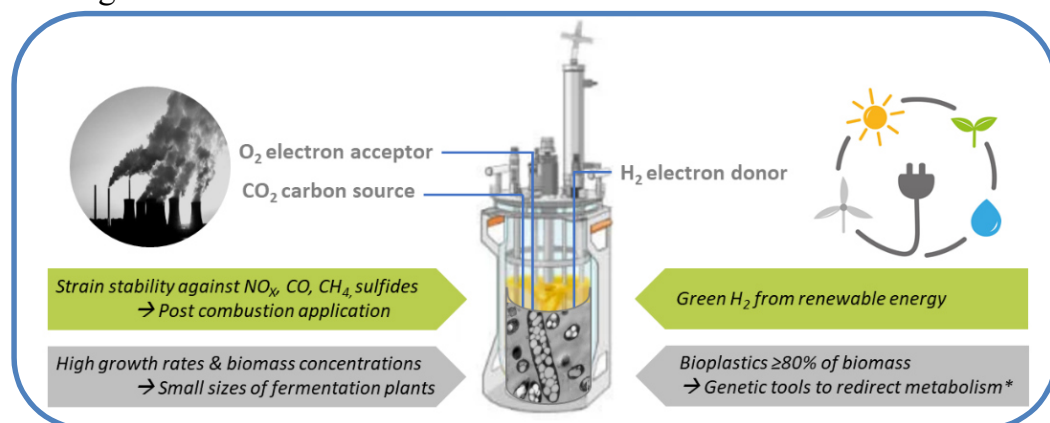
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"Biological carbon capture and utilization (Bio-CCU)" refers to the recycling of CO₂ in chemicals and materials through biotechnological processes. This makes carbon available again as a raw material in a circular economy. Highly efficient hydrogen-oxidizing bacteria (HOBs) obtain the energy required for the assimilation of CO₂ by using H₂ and O₂ as electron and energy donors, respectively. Among them, *Cupriavidus necator* (also known as *Ralstonia eutropha*) is considered a potential game changer for biological CO₂ utilization, as it is able to convert excess CO₂ into the microbial storage material polyhydroxybutyrate (PHB) (in amounts of up to 82% of the dry weight of the cell).¹ The metabolism is genetically tractable,² and alternative products from CO₂ such as customized polyhydroxyalkanoates or versatile organic solvents become available. The development of bio-CCU processes based on HOBs is however hampered by difficulties in handling the gaseous substrate mixtures (O₂, H₂, CO₂). Here we will discuss the O₂ sensitivity of HOBs and the impact of explosive substrate gas mixtures on process design.^{1,3}



Knallgas fermentation of Cupriavidus necator in a nutshell.

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Enzymes in action: understanding the basics of biocatalysis

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Enzymes are Nature's catalysts that facilitate and orchestrate the countless metabolic reactions within living cells. Fulfilling this task requires remarkable catalytic efficiencies (speed) and selectivities, but also efficient controlling and optimization mechanisms. These attributes are linked to the structural features of enzymes: Despite being created from only 20 distinct amino acids, enzymes span several nanometers in size, which enables precise architectural fine-tuning for their specific catalytic task. The field of Biocatalysis investigates the chemical diversity and reaction mechanisms of enzymes and harnesses their capabilities to advance synthetic chemistry.

This lecture discusses the fundamentals of biocatalysis by highlighting the composition and structure of enzymes and the mechanistic origin of their catalytic abilities. Practical applications of enzymes in synthesis will be discussed with a special emphasis on their selectivities. Moreover, the lecture will touch upon recent advancements in biocatalysis, including enzyme engineering and the application of enzymatic cascade reactions.

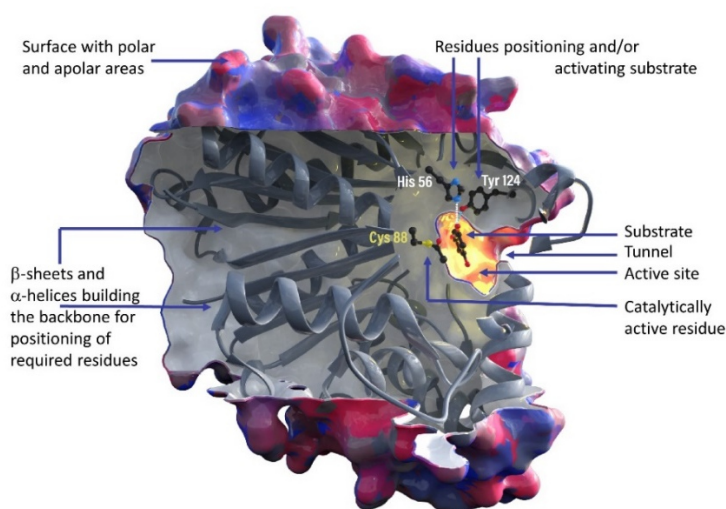


Figure 1: The features of an enzyme, including its surface, its secondary structure elements, the tunnel leading to the active site, the catalytically active residues and the substrate (adapted from¹; PDB: 5MG5).

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Catalysis for a (more) sustainable chemistry, an industrial perspective

Christophe Le Ret



Catalysis per se enables more efficient chemistry. Olefin metathesis, cross-coupling catalysis or stereoselective reduction, among others, have recently contributed to design shorter or more efficient syntheses, generating less side-streams and waste, consuming less solvent or energy. They have thus resulted in more environmentally friendly processes for manufacturing of performance materials, fine and specialty chemicals or active pharmaceutical ingredients.

What is next to improve further? Non-PGM catalysis vs PGM catalysis? Flatten the “chemistree” into a field of chemistries?

Let’s review what makes homogeneous catalysis sustainable and what could help make it even more in the future.





Electrobiotechnology for H₂ production and CO₂ reduction

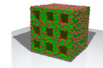
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Biocatalysts have unmatched performance in terms of activity, selectivity and energy efficiency for the conversion of small molecules such as H₂, CO₂, O₂ or N₂. However, implementation of biocatalysts in devices for energy conversion cannot proceed without solutions that mitigate their intrinsic fragility. Protection strategies using a redox-active polymeric matrices can effectively stabilize biocatalysts such as the hydrogenase and significantly increase their operational lifetime for electrocatalytic H₂ oxidation or production [1, 2]. Mass transport and electron transfer limitations emerge as trade-offs when increasing matrix dimensions for protection considerations [3]. Quantitative analysis supported by kinetic modeling enable to pin-point such bottlenecks and guide the rational design of the immobilization matrix [4, 5] to enable high catalyst utilization that can theoretically provide robustness for non-limiting periods of time even when using highly fragile hydrogenases [6, 7]. Engineering catalytic reversibility [8] into the redox-active films embedding the hydrogenase enables H₂ oxidation and H₂ evolution at minimal overpotential, making the protected hydrogenase energy efficient in fuel cell and electrolyzers [9]. The same redox-active films were also successfully applied to construct energy efficient biohybrid systems based on CO₂ fixating enzyme [10]. We show that fine tuning of the reduction potential of the polymer is a prerequisite for both bidirectionality and protection under intermittent use.

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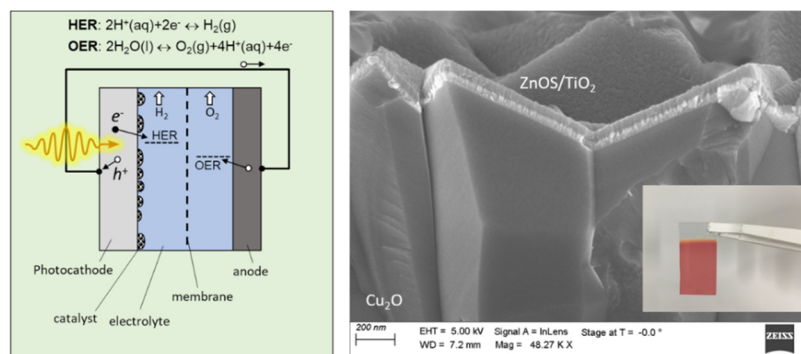
Photoelectrochemical water splitting

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Photoelectrochemical (PEC) water splitting is a process that uses light to split water into hydrogen and oxygen, thereby producing green hydrogen fuel. Key components of PEC devices are the photoelectrodes (photo-cathodes and -anodes), which are composed of semiconductors that absorb light and generate electrical charges, which eventually drive the hydrogen and oxygen evolution electrochemical reactions (HER and OER). The photoelectrodes are immersed in the electrolyte, composed of water with additives to increase its conductivity and regulate the pH. Co-catalysts, mostly based on platinum-group-metal islands, are also used to facilitate the electrochemical reactions.

In a representative PEC process (see Figure), light impinges on the photocathode, generating electron-hole pairs. Electrons migrate towards the photocathode/electrolyte surface where the HER takes place. Holes move in the opposite direction and travel through an external circuit to the anode, for the OER. The overall water splitting process requires a minimum energy of 1.23 eV or 237.2 kJ per mol. To drive the reaction at a practical rate and account for losses, the energy should be >1.6 eV. Semiconductors with bandgap above this threshold are needed to harvest these photons and drive the water splitting reactions. Photoelectrodes need to fulfill other constraints: their valence and conduction band edges need to straddle the HER and OER levels. Additionally, their oxidation and reduction potentials need to be favorably aligned with respect to the HER and OER levels to prevent photo-degradation.



(Left) Schematic of a PEC cell. (Right) Cross section SEM image of a photocathode made of Cu₂O semiconductor and top oxide layers for junction formation and passivation.

Taking under consideration the above constraints, we will review state-of-the-art materials and architectures for PEC devices and evaluate them from the point of view of solar-to-hydrogen efficiency, long-term stability and economic viability on a large scale. To this end, we will also consider aspects of PEC cell design. The competitiveness of PEC compared with commercial photovoltaic-coupled electrolyzers (such as the Proton Exchange Membrane – or PEM – electrolyzer) will be further discussed.



Oral Presentations



Development of a metal-organic-framework encapsulated wholecell biocatalyst

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Hazardous reaction conditions often limit biocatalytic processes. Metal-organicframework (MOF) exoskeletons were successful as a protective shield for mammalian cells against proteases¹, osmotic stress, reactive oxygen species, harmful pH values and UVexposure². MOF encapsulation by biomimetic mineralization bearing protective features was shown for whole yeast cells as well^{3,4}. In this study we combine named findings and explore MOF encapsulation of the yeast *Komagataella phaffii* for whole-cell biocatalysis. Two factors were defined as crucial: 1) metabolic activity and 2) continuous and protective coating. In regard to improved enzymatic activities achieved by multivariate-ZIF-8 enzyme encapsulation^{5,6}, the influence of varying ratios of the organic ligands 2-methylimidazole (HmIM; ZIF-8) and 3-methyl-1,2,3-triazole (Hmtz, MAF-7) on yeast metabolic activity was tested. By combining HmIM and Hmtz in different ratios, the metabolic activity increased from 19% to 61%. Subsequently, successful encapsulation was achieved using an optimized mixed ligand ratio. With our optimized protocol, yeasts displayed >90% metabolic activity. Upon coating, ZIF-8 and MAF-7 typical sodalite topology was verified by XRD analysis. Spatial protection provided by the MOF coating was tested by exposing coated yeast to Zeocin®. Encapsulated *K. phaffii* maintained the same metabolic activity as measured prior to exposure. The combination of spatial protection and high metabolic activity now opens up vast possibilities for MOF application in whole-cell biocatalysis.

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Towards rare-earth-late transition metal catalysts for hydrofunctionalisation reactions

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The chemistry of complexes featuring both early and late transition metals provided insight into aspects such as metal-metal interaction and cooperative reactivity. In contrast to the early transition metals, the elements of the f-block have received significantly less attention. Previous examples were reported by the groups of Kempe and Roesky exploring aspects such as intermetallic bonding.^{1,2} Only recently, Lu and co-workers demonstrated the application of rare-earth-transition metal complexes in hydrogenation catalysis.³

In this contribution, our work on heterobimetallic rare-earth-late transition metal complexes based of supporting phosphinophenolate and -indenyl ligands will be present (Figure 1).^{4,5} For the latter systems, we recently demonstrated its utility to catalyse hydroamination reactions.⁴ Expanding this chemistry to heterobimetallic systems, we investigated heterobimetallic complexes featuring late transition metals such as nickel or palladium. As part of this work, we also investigated the reactivity of these rare-earth-group 10 metal complexes in hydroamination and alkyne oligomerisation catalysis.

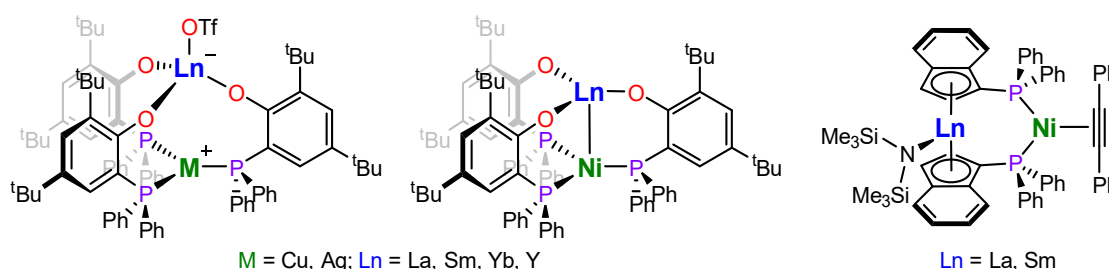


Figure 1. Selected examples of heterometallic rare-earth-late transition metal complexes.

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The epoxy-amine reaction – industrially relevant proton transfer catalysis

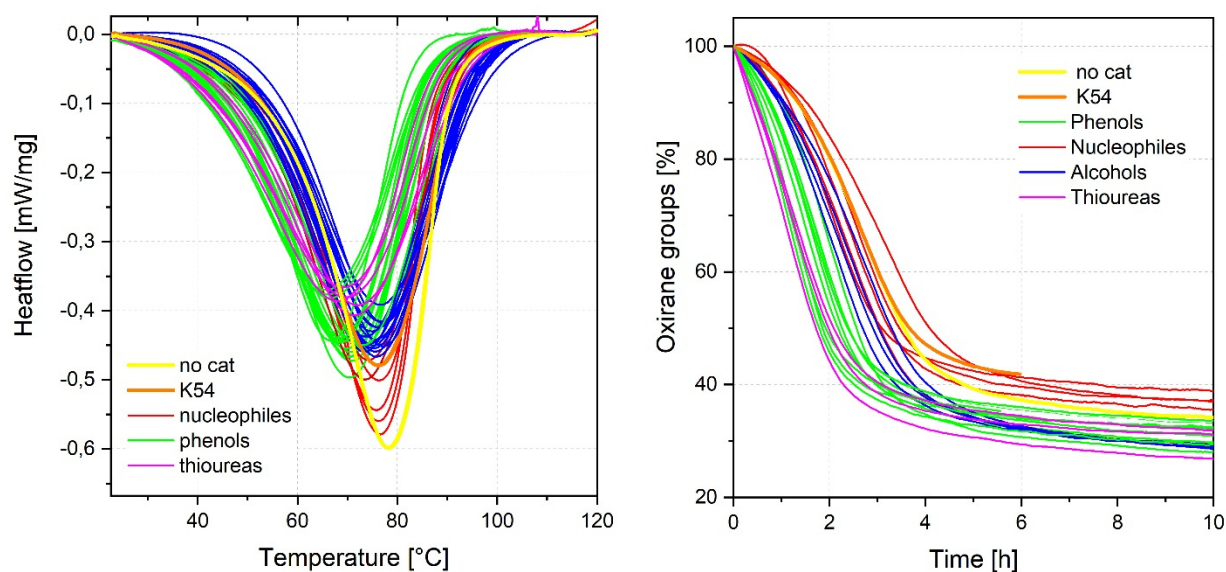
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Epoxy resins are thermosetting materials used in a wide variety of applications such as chemical anchoring, coating applications, electrical insulation and construction in the form of composites. Epoxy monomers are typically cured with curing agents (also called hardeners) such as anhydrides, phenols, isocyanates, thiols and amines. The latter class of curing agents is the most economically important.¹

In this contribution we will discuss the mechanism of the epoxy-amine reaction and show ways to influence the rate of the reaction, thereby revealing the role and mode of action of catalysts² by studying a model formulation consisting of the diglycidyl ether of bisphenol A (DGEBA) and 1,3-bis(aminomethyl)cyclohexane (BAC).³



left: dynamic DSC measurements (heating rate: 2K/min) and right: IR reaction monitoring (ATR-mode, 30 °C) of formulations made of DGEBA : BAC = 1 : 0.5 with or without 0.05 equiv. of the respective additive.³

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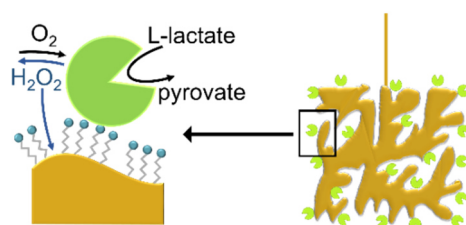
Influence of self-assembled monolayer functionalization on nanoporous gold - lactate oxidase electrodes with different pore-sizes

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Biocatalytic sensing devices, such as enzyme electrodes are subject of intensive research as they combine the highly selective catalytic behaviour of enzymes with the ability to monitor and control the reactions electrochemically. In a similar manner to conventional non-conductive carriers, electrode materials with a high surface area are sought after, as it allows for the immobilisation of a greater quantity of enzyme. Nanoporous gold (npAu) is therefore an especially suitable material, offering a high surface-to-volume ratio, good conductivity and biocompatibility. npAu electrodes can be prepared particularly well by electrochemical dealloying, a process that removes the less noble component from a master alloy.¹ The material's pore size can then be readily adjusted through thermal annealing. To create reliable bioelectrodes, it is essential to gain a fundamental understanding of the immobilization behaviour of enzymes on nanoporous metal. Therefore, the well-studied L-lactase oxidase (LOx) from *Aerococcus viridans* was chosen as a model enzyme. LOx catalyses the oxidation of L-lactate while reducing oxygen (O₂) to hydrogen peroxide (H₂O₂), which can further be detected electrochemically at the electrode's surface, making it potentially useful for medical as well as for food industry applications. To enable immobilization on gold, an interlayer between metal and enzyme is required, which is provided by modification with self-assembled monolayers (SAMs). The specific functional groups of the SAMs (such as sulfonic acid, carboxylic acid, or amine groups) influence the amount of adsorbed enzyme and therefore the activity of the npAu-enzyme hybrid electrodes. Despite the fact that LOx at neutral pH is known to have a negative surface charge,² the highest catalytic activity is observed on npAu electrodes that carry a strongly negatively charged SAM as well. In addition, also a strong pore-size dependence was found for this system. This behaviour is discussed in terms of immobilization mechanisms as well as stability on the different surfaces.



Schematic representation of the operation of a npAu-LOx electrode

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MTV-MOF biocomposites: tuning hydrophobicity for enhanced enzymatic performance

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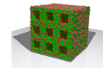
Metal-organic frameworks (MOFs) are extended materials with porous reticular structures¹ synthesized by a modular approach involving inorganic centers (metal ions) bridged by organic constituents (linkers)², featuring high surface areas, adjustable crystalline symmetry, and versatile pore chemistry.^{1,2} Multivariate MOFs (MTV-MOFs) incorporate different constituents as building blocks while maintaining material periodicity¹, optimizing the pore environment, and enhancing tailored properties³ like MOF hydrophobicity.^{3,4} Metal Azolate Frameworks (MAFs), a subclass of MOFs, can utilize the MTV-approach.³ Two widespread examples of MAFs are ZIF-8, composed of Zn²⁺ cations and 2-methylimidazole (2-HmIm) ligands, which is hydrophobic, and MAF-7, assembled from Zn²⁺ cations and 3-Methyl-1H-1,2,4-triazole (3-Mtz) ligands, which is highly hydrophilic.⁴ Both MOFs can be used for enzyme encapsulation, protecting enzymes from environmental and harsh conditions.⁴ In particular, MOFs have been suggested to immobilize lipases such as *Candida rugosa* lipase (CRL) to enhance its sensitivity and robustness for detecting organic pesticides and herbicides.^{5,6} However, current research efforts are needed to develop synthesis protocols that enhance the MOF-biocomposite's activity and eliminate the need for potentially detrimental additives, such as ammonia, which is typically required for the synthesis of MAF-7 biocomposites.⁴ In this work we apply the MTV-approach for the synthesis of CRL@MTV-MAF-biocomposites using two distinct ligands, 2-HmIm and 3-Mtz, leading to an isorecticular structure. We studied the interaction between CRL and the MTV-MAFs, by evaluating different ligand ratios and analyzing their impact on crystallinity, enzymatic activity, encapsulation efficiency and crystal structure, with the aim of improving the biocomposite's performance. This study reveals a non-linear trend between the enzymatic activity of CRL@MTV-MAF and the MOF-matrix's hydrophilicity, where the highest achievable activity is 41% higher than that of the free enzyme, and without using ammonia. This progress in the development of additive-free highly active CRL@MTV-MAF systems will enable their use in different applications.

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Poster Presentations



Structural characterization of nanoporous copper

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Nanoporous metals are generally defined as metals with features in the pore structure in the range of 100 nm or less. Nanoporous copper (np-Cu) has recently attracted attention as an alternative to nanoporous gold or platinum. Our np-Cu is prepared by a three-step process: (i) in-situ alloying of aluminium/copper by laser powder bed fusion, often referred to as the 3D laser printing process, (ii) subsequent annealing at 530° C, followed by (iii) a de-alloying process to remove the aluminium from the bulk alloy. The properties of np-Cu including morphology, crystal structures and chemical composition were systematically characterized by X-ray diffraction and X-ray fluorescence spectroscopy while topography and composition of the surfaces were investigated by scanning electron microscopy (SEM). In addition, the pore size distribution and internal surface area of np-Cu are quantified using techniques such as microcomputed tomography (μ -CT) and mercury intrusion porosimetry. Although the composition of the domains in the alloy changes during the de-alloying process, these domains retain their spatial position and extent.



Noble-metal free photocatalysis – nickel sulfide modified titania for solar hydrogen generation

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The endeavor to meet the ever-growing energy demand employing renewable sources makes the development of technologies for their efficient utilization crucial. An important field of research is the solar-powered generation of chemical fuels such as hydrogen. The nontoxic, cheap, and abundant photocatalyst TiO₂ is promising for this application, but suffers from low utilization of visible light, a large hydrogen evolution overpotential, and fast charge carrier recombination.¹ Therefore, the use of cocatalysts is necessary, which enhance light utilization by adjusting the band gap and improve charge carrier separation. Currently, mostly noble metals are used, but replacing them with metal sulfides can significantly lower the cost. We modified mesoporous titania films with a thin layer of nickel sulfide using nickel xanthates as single-source precursors. Xanthates provide a simple method to prepare homogeneous metal sulfide films with tunable stoichiometry, phase, and morphology, depending on the xanthate's ligand.² We prepared and characterized a range of different nickel xanthates and evaluated the photocatalytic performance of our modified catalysts using hydrogen evolution experiments with methanol as sacrificial electron donor. The hydrogen evolution experiments demonstrated a significant increase of the efficiency for the NiS modified films compared to the pristine titania. The best performing catalyst reached a hydrogen production rate of 3.0 mmol h⁻¹ g⁻¹ (290 times the efficiency of pristine titania) over a duration of 20 hours, which is comparable to values reported for the titania/nickel system applied in suspension.³

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Fabrication of nanoporous copper as carrier material for metalenzyme hybrid electrodes

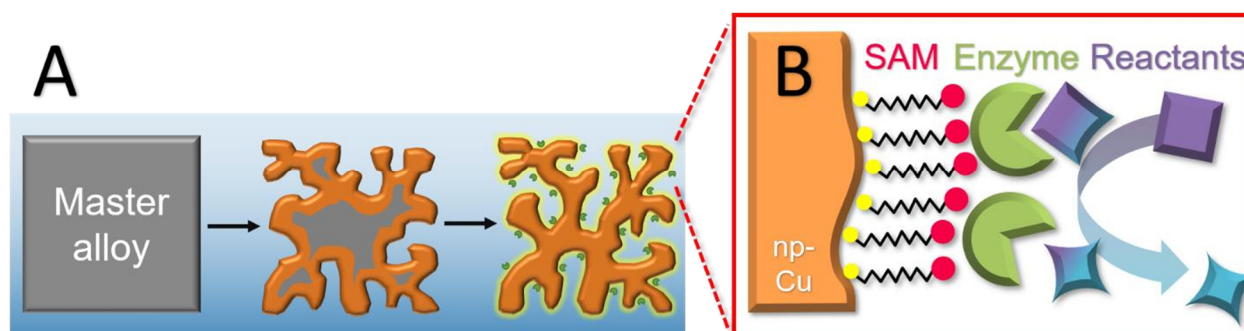
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Metal-enzyme hybrid electrodes present a compelling way to use biomolecules bound to a conducting substrate for highly selective applications in sensing and catalysis. Exploiting the high surface area of nanoporous metals reduces the amount of needed noble/rare metals for catalysis. The most studied metal-enzyme hybrid systems are based on gold as the carrier material, which is functionalized using an organic interlayer between the metal surface and the enzyme as shown in the schematic below.

In order to provide an alternative using more abundant raw materials, we present the fabrication of copper-based carriers for metal-enzyme hybrid electrodes following this concept. Nanoporous copper carriers are created by electrochemical dealloying, a selective etching process in which the less noble element of a master alloy is dissolved. We investigate the dealloying behavior of different copper alloys, and compare the nanoporous copper samples to the well-known Au-Ag system. In addition to electrochemical characterization, in-situ resistometry allows a more in-depth analysis of the dealloying process,¹ which for copper is strongly influenced by the formation of oxides. These oxides in turn can be functionalized and also provide more favorable surface conditions for enzyme stability.²



Concept of a copper-based metal-enzyme hybrid electrode. A Nanoporous copper carrier is fabricated by dealloying of a precursor alloy. B Copper surface is functionalized with organic linkers self-assembled into a monolayer structure (SAM), onto which enzymes are immobilized to enable enzymatic biocatalysis.

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Photoresponsive covalently linked dextran networks – towards functional hydrogels

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Functional materials that can take up and release guest molecules upon stimulation with light can find applications in the area of targeted drug release.¹ Such systems are often based on azobenzene, a molecular photoswitch that can be photoisomerized between its cis and trans isomers.² The bacterial polysaccharide dextran and its modifications have been used in a wide variety of drug delivery systems.³ Here a previously unreported doubly-covalent ester link by azobenzene moieties opens the way for a photo-triggered porous device for the release and capture of small molecules. We have been exploring the potential of such materials by varying the degree and fashion of crosslinking. The preparations of photochromic “functional” hydrogels *via* this procedure has been demonstrated.

Control experiments indicate remarkably different material properties when the azobenzene linker is attached by one or two covalent bonds. We have been following the kinetics of trans↔cis isomerizations of the azo-moiety and the micro- and macroscopic properties of the crosslinked dextran network using a wide variety of analytical techniques, including time-resolved UV/VIS spectroscopy, NMR spectroscopy and rheological measurements.

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Optical oxygen sensing with luminescent (surface-anchored) metal organic frameworks

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Porphyrin derivatives constitute excellent building blocks for Metal Organic Frameworks (MOFs), providing thermal stability, permanent porosity and high accessibility to gases with retention of the typical photophysical properties of the porphyrins. Therefore, porphyrinic and other MOFs have emerged as a promising class of sensing materials including those for oxygen measurement. Especially PCN-224, built of Zr₆ clusters and metal(II)-tetrakis-(4-carboxyphenyl) porphyrin (M(II)TCPP, M = Pt, Pd), was found to have promising oxygen sensing properties.¹

Herein, we report novel crystalline MOFs with new porphyrinic building blocks bearing electron-withdrawing substituents, showing promising sensitivity towards oxygen. In addition, Surface-Anchored MOFs (SURMOFs) consisting of Pt(II)TCPP and Indium-Oxo clusters were fabricated on functionalized glass and flexible poly(ethylene terephthalate) supports coated with a thin Indium-Thin-Oxide (ITO) film. The layer-by-layer dipping procedure provided SURMOFs immobilized directly on the substrate with a homogenous surface and sufficient stability to allow the measurement of oxygen at trace levels.

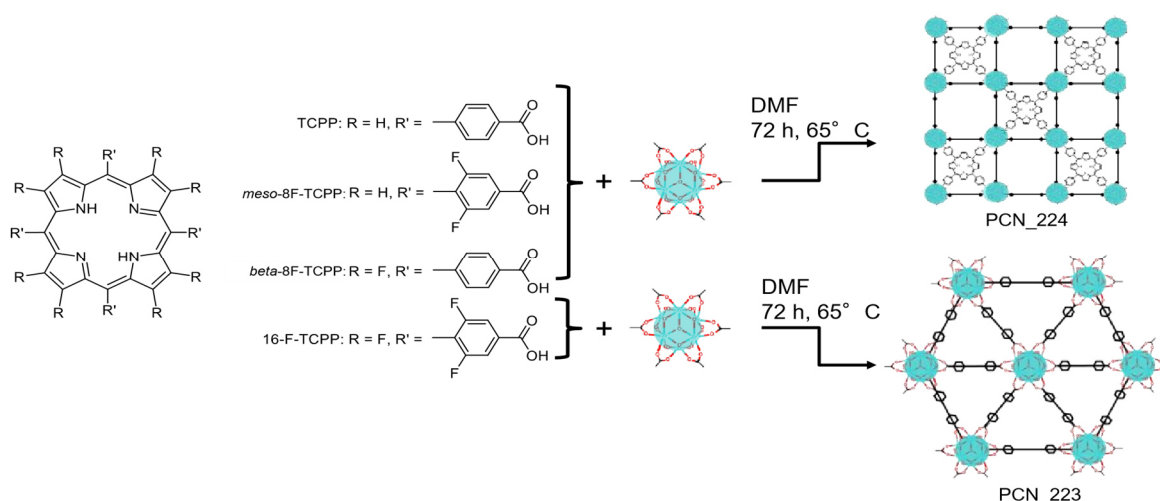


Fig. 1: Formation of Metal Organic Frameworks with partly fluorinated porphyrins as organic linkers.

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Hierarchically porous ZnIn₂S₄ for improved photocatalytic performance

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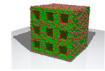
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Enhancing the catalytic activity of photocatalysts is of growing interest in the endeavor to transition towards greener energy resources with a constantly growing demand. In contrast to photovoltaics, photocatalysts utilize sunlight directly for chemical reactions. This can provide the possibility to decompose contaminants in waste water with sunlight irradiation and at the same time generate valuable chemical reagents and so-called solar fuels, like hydrogen. However, in heterogeneous catalysis a huge limiting factor and focus of research is, that such catalysts generally show low surface areas and thus low available reactive sites. In this work we used a single source precursor method using xanthates for the synthesis of the established photocatalyst zinc indium sulfide. The xanthate method, which offers solution processible sulfide films, enables us to combine the inherently formed micropores by the thermal conversion of the xanthate with an external templating method like microsphere lithography. This allowed us to combine macropores around 300 nm from the external template with micropores around 1.6 nm from the xanthates to successfully create hierarchically porous zinc indium sulfide thin films.

Moreover, we performed preliminary photocatalytic dye degradation tests with the organic dye Rhodamine B. With these tests we confirmed a 3.3-fold increase in specific catalytic activity of the hierarchically porous thin films compared to the bulk films. These results suggest promise to optimize photocatalytic activity via multiscale porosity.

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Hierarchical porosity in additively manufactured nickel for catalytic applications

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Nickel is a common and well-researched catalyst material with a wide variety of industrial applications. The inner surface area is a critical parameter for the catalytic process as it corresponds to the active sites available for catalytic reactions. We have tried a new approach to increase the surface area by producing Ni catalysts via the additive manufacturing technique of laser powder bed fusion (LPBF). It is possible to obtain a highly porous material by adjusting the printing parameters related to energy input, such as power, laser speed and hatching distance.

The printing angle, which refers to the angle of the laser pathway between two layers, does not directly influence the local energy input, but can, especially in combination with large hatching distances, be varied to introduce hierarchical porosity.

Upon cooling, the melted bulk material creates a matrix of coarse porous structure, while the surface is characterised by a fine-density structure produced by partial sintering of powder particles.

The effects of various printing parameter combinations have been compared by light optical microscopy, scanning electron microscopy and microtomography.



Catalytic demethylation of Kraft black liquor using heterogeneous catalysts

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Lignin is the second most abundant biopolymer on earth. [1] It can also be isolated from black liquor, a side stream generated during kraft cooking which is used for lignin disintegration.

Demethylation of black liquor has sparked industrial interest as the reactive sites of the biopolymer are increased, especially because the concentration of phenolic OH groups increase during demethylation this lignin is more suitable as phenol replacement in resins than unmodified lignin. [2] In addition, precipitation of lignin from Kraft black liquor helps debottlenecking the recovery boiler by decreasing the heat value of the black liquor, which in turn allows higher production without the need for a larger recovery boiler. [3]

Demethylation can be achieved in various ways, for example by heat treatment [3], introducing equimolar amounts of sulphur [4], or homogeneous and heterogeneous catalysis. In this project, the performance of the heterogeneous catalysts CatGuard 20/21, CatGuard 10, Ni76Al24, and copper(I)oxide for the demethylation of lignin present in black liquor were compared to a heat treatment without any catalysts. The demethylation was performed in a batch reactor at 210 °C for two or four hours. After hydrothermal treatment, the black liquor was acidified to precipitate lignin. Further analysis of lignin involved headspace-GC and NIR measurements.

A catalyst basket was developed to ensure adequate mixing and to prevent porous material from clogging the sampling line. All experiments lasted for two hours, except the one with Cu₂O, and the heat treatment reference. While CatGuard 20/21 without the use of the basket showed a slightly better demethylation performance than the heat treatment, this material cannot be used in further experiments as it cannot withstand the harsh reaction conditions of pH 14 at 210 °C and it dissolves. The other catalysts (Cu₂O, Ni76Al24, CatGuard 20/21 in the basket, CatGuard 10) showed no significant improvement. For all experiments, the molecular weight and the methoxy groups showed a decreasing trend over time, while the phenolic hydroxy group content increased.

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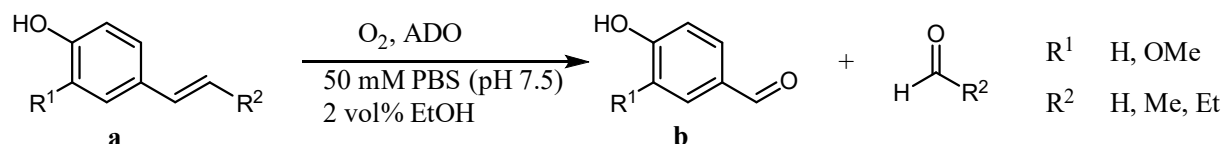
Diversification of carotenoid cleaving enzymes serving as ‘ozonylases’ for generation of aldehydes from a lignin-based feedstock

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Carotenoid cleaving enzymes (CCOs) are non-heme iron-dependent oxygenases that can be used as an alternative to ozonolysis. Unlike ozonolysis, they use molecular oxygen instead of ozone to cleave alkenes to form two equivalents of carbonyl compound (aldehyde or ketone, depending on the substitution pattern of the alkene). The catalytic center is an Fe^{2+} that is bonded by 4 histidine residues. Based on the known enzyme Aromatic DiOxygenase (ADO) from *Thermothelomyces thermophila*^[1] we conducted a sequence similarity search and found several promising enzymes.

A selected set of enzymes was tested in a mono-phasic whole cell reaction to convert several substrates, including 4-vinyl-guaiacol and isoeugenol, to vanillin. Among the tested enzymes, *AspADO* (*Altererythrobacter* sp.), *TsADO* (*Talaromyces stipitatus*), *PaADO* (*Podospira anserina*), *VsADO* (*Valsa sordida*), and *CpADO* from (*Coniochaeta pulveracea*) showed significant yields of product. However, *MapADO* from the marine fungus *Moesziomyces aphidis* was found to be the most effective in converting isoeugenol to vanillin. Using whole cells containing *MapADO*, we achieved quantitative conversion of 60 mM isoeugenol to the corresponding aldehyde overnight. Furthermore, 1 mg/mL of purified *MapADO* converted 20 mM of the same substrate completely in less than 30 minutes.

In conclusion, the novel ‘ozonylases’ produced up to more than 75 times more product compared to the already described ADO.¹

Acknowledgements: This project received funding from FWF (Project No P33687)

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Insights into a bifunctional catalase-phenol oxidase from a marine-derived *Cladosporium* species

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The biodiversity of fungi and their extensive enzymatic wealth have placed these microorganisms at the forefront of contemporary environmental and industrial research. The last decade, marine-associated *Cladosporium* species have gained substantial scientific attention, owing to the production of a wide array of metabolites and the expression of diverse enzymes, pertinent to biotechnological applications [1]. A recent function-based study on the bioremediation potential of marine fungi against aromatic pollutants evinced *Cladosporium* sp. TM138-S3 as a strong candidate for polychlorinated biphenyls removal, and a typical monofunctional catalase was found upregulated under relevant culture conditions [2]. In this study, this catalase—hereafter termed CPO (Catalase Phenol Oxidase)—was recombinantly expressed in the yeast host *Pichia pastoris* and its biochemical and structural properties together with its catalytic potential are being assessed. CPO is a 250-kDa homotetramer of heme *b* containing subunits, capable of hydrogen peroxide decomposition following non-Michaelis-Menten kinetics. It exhibits mildly alkaline pH optimum, mesophilic temperature stability, and halotolerant catalytic behavior. Its side phenol oxidase activity was assessed spectrophotometrically towards phenol, catechol, biphenyls, and select chlorinated compounds. CPO demonstrates clear catechol oxidase activity but absence of cresolase activity, indicative of substrate specificity towards benzene rings with two hydroxy substituents. In vitro inhibition studies appear to support the notion that heme *b* is the active site of the oxidative activity observed [3, 4]. Structural studies on ligand-bound CPO together with more extensive investigation of its catalytic potential are under way. This work provides a fresh view on a long-known class of enzymes and their unexplored capabilities for bioremediation and oxidation of unconventional substrates, as opposed to their traditional uses to the present day.

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