Abstract:

Title of Project: Additive manufacturing (3D printing) of chemo- and biocatalysts with control over spatial composition and dynamic functionalities

Co-supervisor 1: Prof. Dr. Aleksander Gurlo, Chair of Advanced Ceramic Materials, Institute of Materials Science and Technology - TU Berlin

Co-supervisor 2: Dr. Oliver Lenz, Institut für Chemie – TU Berlin

The overall goal of the project is to develop and apply additive manufacturing (3D printing) approach for controlling the spatial composition and dynamic functionalities in chemo- and biocatalysts. To achieve this, a 3D printing approach will be applied to several model systems, ranging from heterogeneous catalysts (e.g. mesoporous silica loaded with bi-metal nanoparticles; Ru-Rh / solid phosphine ligands model systems) to biocatalysts (e.g. [NiFe] hydrogenases and other enzymes). The shape design freedom of additive manufacturing provides a unique opportunity in developing chemo- and biocatalysts with tunable functionalities. In the first line, the following fabrication methods will be applied: (i) stereolithography with hydrogels, and (ii) Direct Ink Writing with colloidal suspensions.

Extended version of the project:

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1. Overall goal of the project

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2. State of the art

Additive manufacturing (AM) is defined as 'a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies' according to the American Society of the International Association for Testing and Materials (ASTM F2792-12a). In the last years, AM has dramatically developed and grown into diverse processes, including stereolithography (SLA), fused deposition modeling (FDM), selective laser sintering (SLS), selective laser melting (SLM), laminated object manufacturing (LOM), inkjet printing, and others. Nonetheless, the general foundation of the various AM technologies is similar. First, the three-dimensional model is generated with a computer-aided design (CAD) and sliced into finite numbers of two-dimensional (2D) layers. Then by building these 2D layers one by one, a three-dimensional object can be obtained. Theoretically, any object with complex 3D geometry can be fabricated in this manner. AM is distinctly different when compared to traditional manufacturing processes, such as machining, casting and forming, as it provides a cost-effective way to build complex shaped parts. The advantages of AM include: (i) the easy realization of customized and personalized designs, where changing the final product geometry only requires the modification of the uploaded CAD file, (ii) the material waste is significantly reduced compared to subtractive manufacturing methods, (iii) casting molds as well as shaping/cutting tools are not required during the fabrication process and (iv) most importantly, the AM technology liberates the geometry restriction during fabrication and allows engineers and designers to create novel ideas and structures.

The application of the additive manufacturing technologies in the field of catalysis is still in its infancy. This is especially true both for heterogeneous catalysis as well as for biocatalysis. Recent reviews (*Nature Reviews Chemistry, 2019, 3, 305–314; ChemCatChem, 2018, 10, 1512-1525; Catals. Sci. technol. 2017, 7, 3421-3439*) address in more detail unresolved issues as well as future directions. All agree that AM is highly useful for catalyst exploration and has exceptional potential for broader catalyst exploration if material restrictions can be overcome and multi-material systems can be implemented with other AM technologies.

3. Specific aims and how they may be reached

The objectives of our proposal are:
(1) to develop and explore additive manufacturing fabrication methods for heterogeneous catalysts;
(2) to develop and explore the additive manufacturing fabrication methods for biocatalysts

This project consists of two WP, which focus on one of the objectives stated above.

WP1. Additive manufacturing fabrication methods for heterogeneous catalysts

(collaboration with *Thomas / Schomäcker /Repke*)

The goal is the direct deposition of ceramic slurries in a defined pattern. Direct Ink Writing (DIW, Robocasting) will be applied to assemble 3D complex geometries through extruding an ink consisting of a ceramic paste, highly viscous colloidal suspension or slurry by controlling a nozzle. The ceramic slurry after deposition in DIW or robocasting does not require an additional curing or drying process, as it exploits the shear-thinning behavior of the prepared ink. Ceramic slurries or pastes with high solid loading behave like a high viscous gel when loaded inside the extruder. Upon extrusion through the nozzle, the induced shear stress will break down the gel structure of the ink and significantly decrease its viscosity, which allows the ink to be deposited smoothly. Immediately after extrusion, the ceramic ink is back to static state and recovers its high viscosity, which will preserve the printed pattern and avoid undesired deformation. The main challenge will be to develop suitable ink compositions. Different parameters – that can lead to the shear-thinning behavior of the inks - such as pH value, ionic strength, addition of polyelectrolytes and utilization of polymeric binder and plasticizer will be explored. In the first line, the 3D printing of mesoporous silica loaded with bi-metal nanoparticles will be explored. In the second step the systems with two bi-metallic surface clusters (such as Ru-Rh on solid phosphine ligands model system, *Thomas*) will be explored; herewith a close collaboration with one running EC2 project (PhD student: Benjamin Bischoff) is expected.

WP2. Additive manufacturing fabrication methods for biocatalysts

(collaboration with *Neubauer, Mroginski, Kaupp*)

First, a versatile stereolithographic route, based on VAT photopolymerization, using fast and inexpensive thiol-ene click reactions to 3D print Si-containing thermosets, developed in the Gurlo group will be applied for hydrogel systems with hydrogenases and other suitable enzymes. Our approach is based on the rapidity and efficiency of the employed thiol-ene click chemistry reactions. The AM process can be effectively performed with conventional light sources (such as projectors) on benchtop Digital Light Processing (DLP) printers. Due to their high optical transparency, which minimizes the scattering effects, resin mixtures are further applicable for more sophisticated techniques such as two-photon polymerization and microstereolithography. A polyviologen-based redox hydrogel protects e.g. hydrogenase from high-potential deactivation and oxygen damage. On the other hand, porous architectures, created by 3D printing will allow for more efficient catalytic conversion.

Furthermore, another challenging aspect is to explore three-dimensional (3-D) nanoporous electrode architectures by using complex shapes and geometries achieved with 3D printing. This strategy is supposed to enhance the amount of enzyme loading, to improve enzyme-substrate interaction, and facilitate electron transfer between the enzyme and the electrode. Here, the focus is to develop prototypes and to evaluate different reactor designs (device configuration). A range of electrodes, with different pore diameters and pore length, will be prepared by printing techniques and the effect of their geometries and arrangement on the enzymatic systems will be investigated. Different enzyme immobilization strategies will be investigated, including mere adsorption, covalent attachmen and by 3D printing of composite systems. Electrochemical, microscopic, biochemical and spectroscopic techniques accessible through collaborators network will be used for system characterisation. In addition, the mechanism of redox reaction performed by the enzyme can be investigated by computational modelling (quantum and molecular mechanics) in cooperation with other groups (*Mroginski, Kaupp*).