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Welcome from the Organizers

It is our great pleasure to welcome you to the 4th Vienna young Scientists Symposium (VSS 2018, 7th and 8th of June). The VSS was launched in the year 2015 as a forum for young researchers. Its focus lies on the communication and exchange of information of young researchers' present scientific projects and working environments. Besides an excellent opportunity to practice and improve one's skills, it finds its larger scope in (interdisciplinary) exchange and the valuable chance to initiate cooperative development of innovative technologies.

Traditionally, the symposium focuses on the main research areas of TU Wien; anyway, it is open to areas beyond these and shows the individual's ability to re-orient and re-present its own work in an interdisciplinary focus. Because the term of information itself, its capture and its exchange, are keywords in the description of the universe's heaviest entities over our societal achievements to the submicroscopic scales of physics, this year's core themes are:

- Industry 4.0
- Intelligent data systems
- Smart and nouvelle materials

Information plays a big role in every of those these and 56 excellent peer-reviewed contributions have found their way into this year's proceedings. Everyone is welcome to participate in the VSS 2018, to discuss the scientific contributions and to exchange ideas in an interdisciplinary manner in vivid discussions with a broad academic audience. If we are able to boost collaborations among faculties, which all are of societal and scientific relevance, we have reached our goal.

The organizing committee wishes you a cheerful and rewarding VSS 2018!

Welcome by the Rector
and the Vice Rector for Research and Innovation

The Vienna young Scientists Symposium (VSS) is a platform, which aims at bringing highly talented individuals and promising projects together, thus demonstrating our students' enthusiasm both for broadening their own scientific horizons and for thinking outside the box, as well as their internalized interdisciplinary perspective. This initiative serves to enhance scientific research, broadens the findings of research groups and strengthens partnership with industry. The impressive volume of the abstracts compiled here rather eloquently conveys the creativity of our students and young scientists, as does this fantastic event itself.

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Scientific work at TU Wien is mainly covered by the five research focal areas of the TUW research matrix, which itself via the embedded research fields is a showcase of TUW scientific expertise.

The VSS 2018 presents research results in the fields of "INDUSTRY 4.0 – From Smart Factory to Smart City", "Novel and Smart Materials" and "Intelligent Data Systems". All these interdisciplinary topics provide vivid evidence of the existing TUW research network.

We would like to express our gratitude towards the organizers and supporters of VSS, who contributed to realizing an outstanding event. Our young scientific talents play an important role in the research advancement for the "TU Wien of tomorrow".

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Research Field *Intelligent Data Systems*

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Introduction

Modern ICT technologies such as Cyber-Physical Systems (CPS), Internet of Things (IoT), Big Data, Cloud Computing, are reshaping the way we perceive, interact and understand our own physical world. For example, CPS consist of tightly intertwined physical and software components that enable to monitor and control the physical environment, while IoT provides the necessary networking infrastructure and services supporting machine-to-machine interoperability and machine-to-human interaction. These systems typically generate an incredible amount of data collected through their distributed sensors. Big data techniques are fundamental to analyze these voluminous and complex datasets, while cloud computing provides on demand computing and storage resources required by these computationally and data intensive tasks. These technologies are now playing a key role in several application domains ranging from manufacturing processes to personalized medicine. With the progress of technology and solutions in each of these fields there is an increasing demand on formal methods for specification languages, verification techniques, and artificial intelligence algorithms to make them smarter and to ensure important safety and security requirements.

Our goal in this symposium is to seek for topics where we see the impact of CPS, IoT, Big Data, Cloud computing, Artificial Intelligence, Formal Methods, etc. on the design, development and operation of intelligent data systems in various domains. We seek for interesting ideas and techniques not only to show the embedment of advanced ICT into these domains, but also how IoT, Big Data, AI, Formal Methods etc. improve these domains through intelligent mechanisms, autonomous monitoring, adaptation and analytics.

The list of the topics:

- Machine learning and big data systems
- IoT and data analytics tools
- Social-cyber-physical-systems
- Artificial Intelligence methods & algorithms
- Intelligence Amplification methods & algorithms
- Formal methods for designing, analyzing and verifying systems

ARTIFICIAL AGENTS IN SOCIO-TECHNICAL SYSTEM

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INTRODUCTION

Self-driving cars, smart ambient home systems, industrial and service robots are all examples of cognitive computing systems that are designed to recieve, analyze data and carry out actions without human intervention [1]. Designing these systems goes beyond the technical domain of simply being intelligent and connected, as their repercussions of the social, organizational and user issues become extremely difficult to ignore [2]. While technological advances have made it possible for the passive objects to become agentic, disagreements persist about the notion of machine agency. This conceptual paper provides an initial typology of artificial agents and reflects the socio-cultural consequences encountered in interacting with artificial agents.

FUNDAMENTAL OF THE PROBLEM

Current developments in the field of artificial intelligent suggest an increase in the agency of machines, with artificial agents taking over control that would have been in the hands of human agents. Agency is defined as “the capacity, condition, or state of acting or of exerting power; a person or thing through which power is exerted or an end is achieved” [3]. Indeed, the agency of machines differs from that of the human. While machines have no conscious selection and self-reflectiveness [4.5], some are yet perceived as having agency. Adaptability [6.7], purposeful-looking movement [8], complementary personalities [9], and humanlike appearance [1] are defined features in literatures that contribute to human’s tendency in ascribing (social) agency to machines. We argue that among all these features, autonomy in artificial agents induces sufficient ques of the agency. In AI and robotics, autonomy is described as the capacity to perform tasks interdependently from external control [10.11]. Taking this into consideration, we can define machine agency as delegated authority; artificial agents are bound by the goal function set by the human agent but have (relative) autonomy in their operation and interaction to achieve the pre-defined goals. Furthermore, machine agency is not something pre-made that can be put inside an artefact but will be attributed to them.

Taking together, we conceptualize artificial agents in three different types (directed agent, semi-autonomous agent, and quasi-autonomous agent) using several dimensions. Though these artificial agents are all situated and embodied agents, major differences exist among them in how they control the input-output cycle, pursue their goal and the extent to which they can perform tasks independently (Table 1).

	Directed agent	**Semi-autonomous agent**	**Quasi-autonomous agent**
Control structure	rule-based, algorithmic	Fuzzy, planner	autonomous control
Goal setting	Achievement of the set goal	Adaption within certain limits	Fundamental change of goal is possible
Interaction with real world	Passive to limited sensory capability	Active data collection and mining	Multisensory perceptions

Autonomous capability	Auto-moving/acting	Auto-learning	Auto-organizing
Response selection	Task and context specific	Task variable, context specific	Task and context variable
Example	Thermostat	Self-driving car	"Survivor" [14]

Table 1: a typology of artificial agents

DISCUSSION AND OUTLOOK

Attributing agency to artificial agents causes a vast amount of discussion about the consequences in practice. Since a key aspect in acceptance of the technology is the social factors [12], understanding the social components of human-agent interaction will provide valuable insights not only for designers but also those who co-work with artificial agents. Therefore, to identify directions for future research, the role of artificial agents in the context of social interaction on different levels need to be analyzed. At the micro level, it is important to consider how human agents perceive the interaction with artificial agents as the subjective readiness of human agents to accept this interaction is more relevant than the objective capabilities of artificial agents [13]. Accordingly, at meso level, greater attention shall be given to social dimension of work and collaboration between the agents. Finally, at the macro level, it is necessary to reflect how the social fabric of society is going to change when we construct and perceive the artificial agents as "other", an abstract notion of what society considers good.

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CLASSIFICATION OF 3D POINT CLOUDS USING DEEP NEURAL NETWORKS

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INTRODUCTION

Topographic 3D point clouds provide a good representation of the Earth's surface and objects atop. They can be acquired by active methods (airborne laser scanning, ALS) as well as passive methods (dense image matching, DIM) [1]. To further process these irregular datasets, a per-point classification (i.e. semantic labeling) is necessary. Current classification methods often rely on hand-crafted attributes to describe local point neighbourhoods, which are then fed to a state-of-the-art classifier like a random forest.

On the other hand, deep neural networks (DNN) have recently outperformed most other classifiers in many different fields of application. While a multitude data types can be used as an input, DNNs are optimized for regular data structures such as rasters, whereas the inherent irregular structure of 3D point clouds hamper a straightforward implementation. This work aims to design, train, and evaluate a DNN as a classifier for 3D point clouds from ALS. The points shall be used directly as input for the DNN.

POINT CLOUDS AND DEEP NEURAL NETWORKS

A point cloud is an unordered set of points in n-D space, with a number of attributes for (a subset of) those points [2]. However, input neurons are very much order dependent, as the input attributes are mapped by index. To overcome this problem, point clouds are often voxelized, i.e. transformed into a regular 3D grid structure, where the order of the points is irrelevant. However, this leads to a loss in resolution (i.e. a label is applied per voxel, not per point) and large processing times, especially with sparsely poplulated voxel structures.

In a novel approach, Qi et al. (2017) [3] have shown that it is possible to approximate a general function defined on a point set by applying a commutative aggregation function like an summation or a multiplication. This results in a permutation-invariant feature for the point set:

$$f(\{x_1, ..., x_n\}) \approx g(h(x_1), ..., h(x_n)) \tag{1}$$

In the scope of neural networks, a commonly used aggregation function is the so-called *max-pooling*, where the maximum value of a vector is chosen as a representative. Since factors and bias of the (linear) function h (in Eqn. 1) are trained, the choice of $g(\mathbf{x}) = \max(\mathbf{x})$ is plausible. An alternative choice for $g(\mathbf{x})$ is a (weighted) average function.

DATA

Data acquired by ALS or DIM embraces additional properties: The spatial distribution is mostly close to a 2D manifold, i.e. the Earth's surface, point densities on a large scale can be assumed relatively constant, and they may cover large areas up to thousands of square kilometers.

The data used in this study covers the province of Vorarlberg in eastern Austria. For training and

validation of the classifier, the existing manually edited classification is used, which differentiates the following main classes: Ground, Low -, Medium -, and High Vegetation, Building, and Water. Since bare earth areas consisting solely of ground points are dominant within the study area, a subselection of the dataset was made, limiting the areas used for training to those representing a large variety of classes. The standard deviation of the class frequencies was used as a measure for this variety.

NETWORK DESIGN

The DNN used in this study follows a pyramid based approach following [4]: From the input points, so-called *superpoints* are created by sampling and local neighbourhood queries. For these *superpoints*, a feature is calculated according to Eqn. 1. These *superpoints* represent the next (higher) level on the pyramid. This method of subsampling and feature generation is applied three times, each level with increasing neighbourhood search radii and decreasing number of *superpoints*.

From the highest-level *superpoints*, features are propagated back to the original points by inverse distance interpolation. Finally, a *softmax* regression is applied to classify the points.

RESULTS AND DISCUSSION

First results look promising with an average accuracy on previously unseen data of 76.9%. Especially vegetation can be differentiated from ground very well (up to 98.6%), with some room for improvement on low vegetation in mountainous areas. Buildings are misclassified as vegetation in a limited number of cases. Tuning of hyperparameters and extended training are expected to further improve these results.

CONCLUSION

The study has shown that classification of topographic 3D point clouds on a per-point basis with neural networks without the need for hand-crafted features or voxelization is possible. This leads to multiple further questions: i) How does a pre-trained DNN perform on classification of datasets from a different scanner (i.e. with a different point distribution pattern, penetration and point density) and/or in different landscapes? ii) How well can the DNN discriminate between specific classes, and does a focus on a binary decision (ground/non-ground) significantly improve the performance? iii) What is the impact of the neighbourhood definition in the *superpoint* abstraction layers?

ACKNOWLEDGEMENTS

The DNN was trained and evaluated at the University of Stuttgart on hardware sponsored by NVIDIA.

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MACHINE INVENTION SYSTEMS: A NEW APPROACH TO INNOVATION

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INTRODUCTION

The momentum gained by recent developments in the field of digital transformation and machine learning show an increasing potential not only to replace dull, dirty or dangerous jobs [1], but also in service and management areas, jobs with self-actualization potential [2]. One area in particular in which new systems are emerging is the generation of new or previously unexplored knowledge and models – i.e. invention. These new types of systems, coined Machine Invention Systems, will be explained in more detail, at first through examples and then through brief theoretical considerations in the following sections.

CURRENT APPLICATIONS

In order to create a better understanding on the nature of these systems and to exemplify their abilities, a cross-industry list of current applications has been compiled (Table 1). Due to the novelty of the field and the lack of a clear denomination for such systems until now, the following examples represent only the few applications that have been validated to contain – partially or totally – machine invention systems.

In the field of Robotics, in order to achieve physical locomotion without any indication on how to achieve it, Darwin [3] uses simulated neuronal networks to 'imagine' how movements should be done and then with the use of a secondary neuronal network perform the movement. In the field of virtual locomotion, DeepMind presented a system[4] that can achieve locomotion under a series of constraints and exhibited an ability to optimize and adapt its movement given no set of rules on how to do so.

Category	Field	Application
Robotics	Physical Locomotion	Darwin
	Virtual Locomotion	DeepMind Locomotion
Defence and Security	Aircraft manoeuvres	LCS Fighter
	Cybersecurity	LCS Cybersecurity
Fine Arts	Musical Composition	Kulitta
	Image Creation	CNN Imaging
Cognitive Science	Quantum Physics	Melvin

Table 1: Overview of the current applications of Machine Invention

In the Defence and Security category, a Learning Classifier System based on a genetics-based machine learning algorithm[5] is used to find best-expected-result manoeuvres to counteract enemy fighters. Also in this category, Learning Classifier Systems can be used to search continuous streams of data for potential threats[6], learn and improve their detection models in order to allow for a fast and steadily evolving detection mechanism.

In Fine Arts, there are musical composition programs like Kulitta[7] that can develop new and unique music scores based on a multi-stage approach machine learning algorithm. On the visual side, Convolutional Neural Networks have demonstrated an ability to interpret images and create new and unique renderings of existing objects and features[8].

Finally, in the field of quantum physics, a topic that resists human logic often, an algorithm called Melvin[9] can devise new viable experiments based on its own generated models that further our understanding of the field.

THE CONCEPT OF MACHINE INVENTION SYSTEMS

Although these applications stem from a large variety of fields, their commonalities allow for the development of a concept. One important observation is that all the above applications exhibit some form of machine learning. However, what differentiates these systems from common machine learning systems is their output. Rather than limiting themselves in finding hidden linkages between factors, or creating statistical analyses on the available data, they use these solutions to generate higher-level models and solutions and test them accordingly. Figure 1 presents the current model of the machine invention systems, together with its most important attributes.

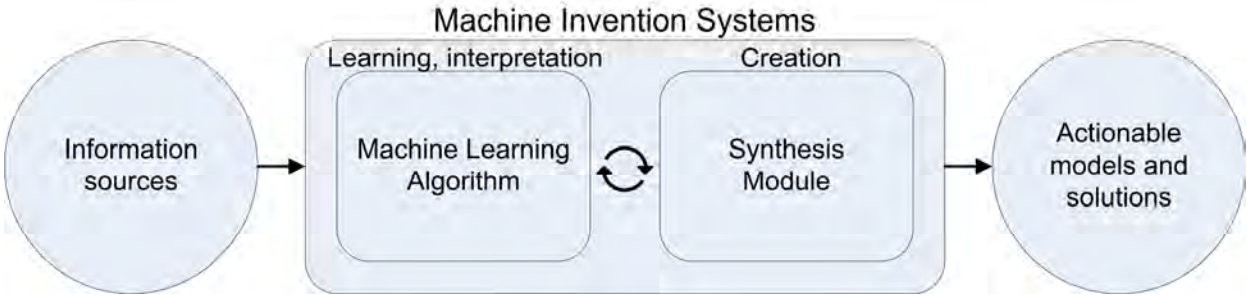

Figure 1: Block diagram of the Machine Invention Systems

Based on the available data and the current development of the model, we can propose that machine invention systems are cyberphysical or virtual systems that can create actionable models and innovative solutions by processing and deriving higher level concepts and models from unorganized information sources.

OUTLOOK

Current efforts focus on understanding what the different categories of machine innovation systems are and what opportunities and challenges are faced by these systems. Furthermore, investigations on the optimal conditions for integrating these systems into the production environments are planned, as well as ethical and societal implications of the knowledge wealth generated by them.

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SIMULATING THE HEART USING MAXELER DATFLOW SUPER-COMPUTING AND FPGA

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INTRODUCTION

Within the scope of the Cyber-Physical Systems Group of the TU Wien my diploma thesis introduces a new approach for cardiac cell simulation. Cardiac cell simulation can be used to test medical monitoring systems, like pacemakers. Hereby it is possible to provide early diagnosis of cardiac arrhythmia.

Despite the great effort to implement efficient GPU-based and CPU-based simulators for different mathematical models, the analysis and the prediction of the cardiac dynamics remains still a very computational task. The aim of our work is to investigate how to use data-flow hardware-based solutions, using Maxeler Dataflow Techology, to improve further the simulation of different cardiac models.

PROBLEM DESCRIPTION

The aim of this work is to gather information about the advantages and disadvantages of using Maxeler Technology to simulate cardiac cells. Therefore given implementations of cardiac cell models, are re-implemented using Maxeler Dataflow.

This will allow a detailed analysis of the resource efficiency and probable optimization. Furthermore, to get statistically relevant results, the obtained simulations will be compared to the ones obtained using other hardware solutions such as using GPU, FPGA and CPU. Furthermore, we aim to evaluate the advantages and disadvantages of using Maxeler Dataflow Technology. Despite the possible benefits, it has to be determined if the complexity of cardiac cell simulation exceeds the scope of what is possible with this technology. To do so, the implementation of cardiac cells is split into three steps. The first step is to implement a single cell of the given model. Building on that, the second step is the implementation of a cell cable according to the cable theory of cells, see [3]. The last step is the simulation of cardiac tissue, represented as multidimensional model.

Based on the implementation in Maxeler Technology several tests with respect to performance, power and memory consumption will be performed. The results of these tests will be set against the values of known state-of-the art technologies. Another part of the evaluation is the comparison of the different models. These will be analyzed regarding their mathematical complexity and realizability in Maxeler Dataflow. Furthermore, the performance, power and memory consumption of the different models in Maxeler Dataflow will be compared.

Additionally this thesis will provide the relevant background information regarding Maxeler Technology, cardiac electro-physiology and other technologies used for simulation.

CURRENT STATE AND EXPECTED RESULTS

The results of the work include a full implementation of a single cell, a cell cable and cardiac tissue in Maxeler Dataflow Technology. Furthermore, as several mathematical models will be implemented, they will be analyzed and compared regarding complexity and performance. The results will be provided as tabular overview, with respect to known benchmarks. As the structure from dataflow application generally differ from control flow applications, the whole structure of the given implementations has to be modified for a working and possible ideal result. In the thesis, the differences of data flow and control flow will be presented, focusing, among others, on the advantages and disadvantages of these architectures.

CONCLUSION

The highly parallel computations generated by Maxeler Dataflow Tchnology allows an acceleration of complex calculations. Such calculations include the simulation of mathematical models of excitable cells. These simulations are important in medical research to provide deeper insight into the causes of certain diseases. Based on this, new preventive measures can be developed. In the work presented, the focus is on cardiac cell simulation and cardiac arrhythmia. Nevertheless technology can easily be adapted and used for other cell types, like neurons. Furthermore the technology can be used to accelerate machine learning algorithms and neural network based AI algorithms, which presents a broad area of application. Further examples of the possible usage of Maxeler Dataflow Technology are provided in the Maxeler App Galary [4].

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CONTROLLED AUTO-ADJUSTMENT OF CONSTRUCTION DETAILS VIA BIM-ENVIRONMENTS AND PARAMETRIC MODELLING

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INTRODUCTION

Building Information Modelling (BIM) is commonly understood as a holistic approach to support the generation and management of digital (and semantically enriched) representations of physical and functional properties of (parts of) the built environment. As compared to conventional CAD (Computer-aided Design) environments, a fundamental feature (and a key advantage) of BIM applications is that the representations are modified and controlled via property settings, not via mere drafting-oriented geometric views (e.g., wireframe line models). However, BIM objects of constituting building parts, which are sorted in so-called families, possess only a limited set of degrees of freedom where and how they might be situated in a building representation. Adapting an object to a construction or installation context still has to be performed by a human user. It this context, it is important to realize that there are normative rules for many building constituents that might be integrated in BIM-environments via algorithms. The present contribution illustrates a case study pertaining to windows and their representations in a common BIM modelling tool. Thereby, the coupling of a parametric modelling environment with BIM is explored in view of an automated approach to context-responsive object attribute adjustment.

WINDOWS AND PARAMETRIC MODELING

As (transparent) parts of the building envelope, windows possess specific characteristics in terms of light and energy transmittance, operability, and thermal and acoustic characteristics. Moreover, in the timeframe and construction logistics of building envelopes, windows hold a special position: They interface to both building shell and to the interior construction. Thus, windows require special attention in the building planning process. In contemporary BIM tools, windows and their components come as families, and thus can be conveniently positioned within a BIM model. However, there is regularly a certain amount of manual adaptation work needed in the BIM-environment to fulfil the requirements of different standards pertaining to structural stability, thermal performance, thermal bridge mitigation, water proofing, user comfort and safety, and maintainability of the windows. In many cases, different windows in the same building share a number of attributes, but differ in others. Human planners are thus forced to check these components manually one by one, even if copy and paste or multi-copy routines exist. Changes in the properties often are caused by different window sizes and orientations. If families are not properly interlinked, it might be required to not only change the properties of a window, but also the characteristics of connected components, such as connected foils, dimensions of window sills, or water proofing components in the window/wall joint. As many of these changes follow standards (e.g., window frame dimensios, which are influenced by different window sizes), partial automation of the related processes could provide effective support for planners.

A PARAMETRIC MODELLING APPROACH

Many BIM and CAD environments offer support for parametric modelling plug-ins (e.g., Dynamo in case of REVIT). To facilitate (partially) automated window properties adjustment (and properties of adjacent components), it was required to first identify the properties that are prone to modification in case of a change of window size, orientation, or positioning. Thereby, the focus was on size-related property changes. In a second step, the dependencies of properties were identified and sketched. Subsequently, these dependencies were modelled in DYNAMO. These algorithms were then subjected to extensive testing. For any BIM model with window families, these algorithms can be connected to the basic model. The relevant workflow for planners is illustrated in Figure 1. Figure 2 illustrates the graphic overview of the dependencies in the DYNAMO-file.

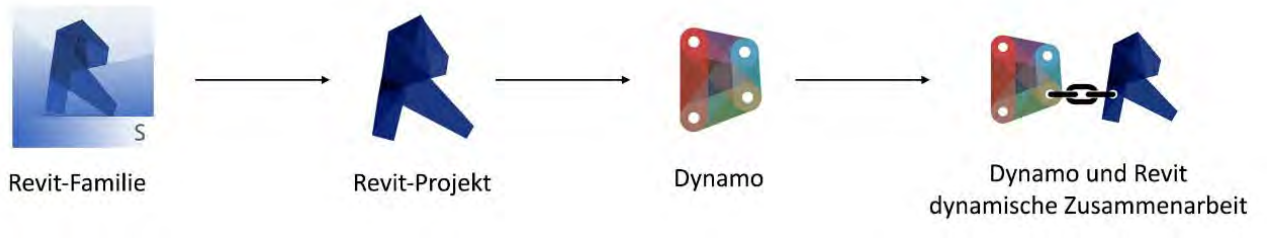

Figure 1: Principle workflow for planners to adopt the parametric change of routines regarding window properties in REVIT/DYNAMO.

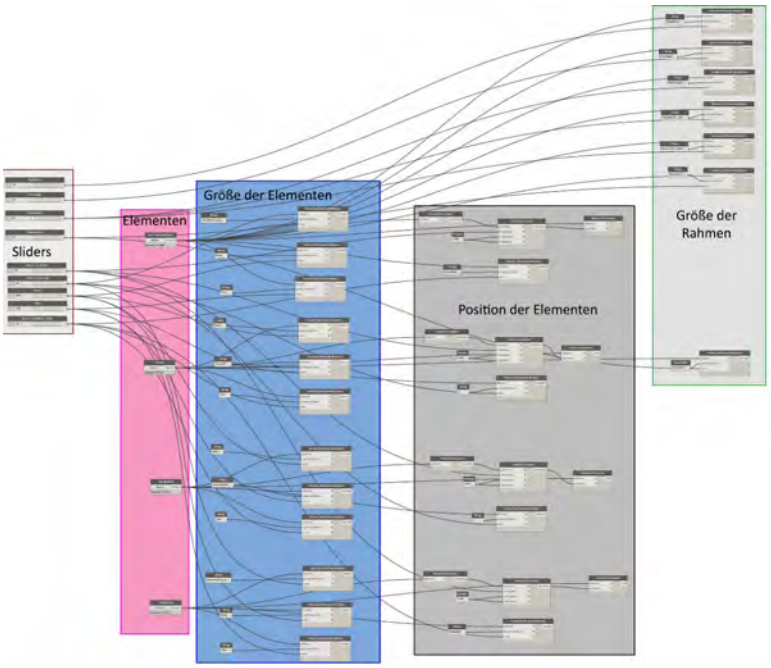

Figure 2: Dependency model in the DYNAMO environment (elements, size of elements, position of elements, size of frame properties).

CONCLUSION

The approach explained above represents an initial attempt to automate the cumbersome change management in BIM models as routinely experienced by the so-called BIM managers. Needless to say, it requires substantial additional work. Nonetheless, it illustrates the large potential of the coupling between BIM tools and parametric modelling environments as applied to the configuration of complex building components such as windows. The next steps include full-fledge modelling of typical window joints and usability testing with interested stakeholders and domain specialists.

CAN FORMAL MODELLING APPROACHES SUPPORT BUILDING PLANING AND PERFORMANCE MODELLING?

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INTRODUCTION

Within building planning processes, regularly a multitude of domain specific aspects need to be considered. These aspects encompass, amongst others, building construction processes, building performance aspects (thermal performance, acoustical performance, ecology performance, etc.), structural stability, and material compatibility. Although the nature of the individual requirements and their normative proof-of-fulfilment procedures is not difficult to grasp, the consideration of all requirements together is non-trivial. Thus, even basic planning tasks require the reasoning capabilities of human experts. However, different stakeholders such as architects, building planners, engineers, or building physics consultants face major challenges while iteratively converging toward design decisions. Aside from being cumbersome and error-prone, “trial and error” processes often result in non-optimal solutions. Given the nature of certain routine working steps in the planning process, intelligent computational support could provide support. In this contribution, we explore the application potential of formal modelling approaches for the AEC (architecture-engineering-construction) domain. Using a case study approach, we outline the methodology and outcome of a number of recently conducted research projects connected with the idea of (partial) automation of routine building planning tasks. Moreover, we review the application potential of certain standard formal modelling approaches in building domain.

CASE STUDY-BASED PROBLEM STATEMENT & APPROACH

Figure 1 (left) illustrates various factors influencing building designs. Many of these aspects do not have an “optional” character, but come with minimum requirements. Regulations pertain to different levels of detail of the building, ranging from large-scale spatial planning over whole building requirements, to single zones, and to building construction assemblies. For instance, the minimum requirements for an exterior wall assembly encompass, amongst others, requirements regarding heat transmission, sound reduction index, vapour diffusion / condensation avoidance, and structural stability (Figure 1, right). The manual creation of assemblies can be understood as easy, if only one of these constraints is looked at. If a number of – partly contradictory - requirements need to be considered, a manual exploration of the design spaces may lead to a rather cumbersome trial-and-error process. Given the numerous possibilities in architectural engineering regarding building construction assemblies, this process can get very time-consuming. Moreover, while the result of this process probably will be a valid combination, it will highly probable be not one close to an optimum. Furthermore, it has to be considered that the generation of building component assemblies not only is performed multiple times for different constructions within an average building delivery process. Rather, today’s planning practice shows the same components modelled repetively in different domain applications (drafting tools, energy certification applications, etc.).

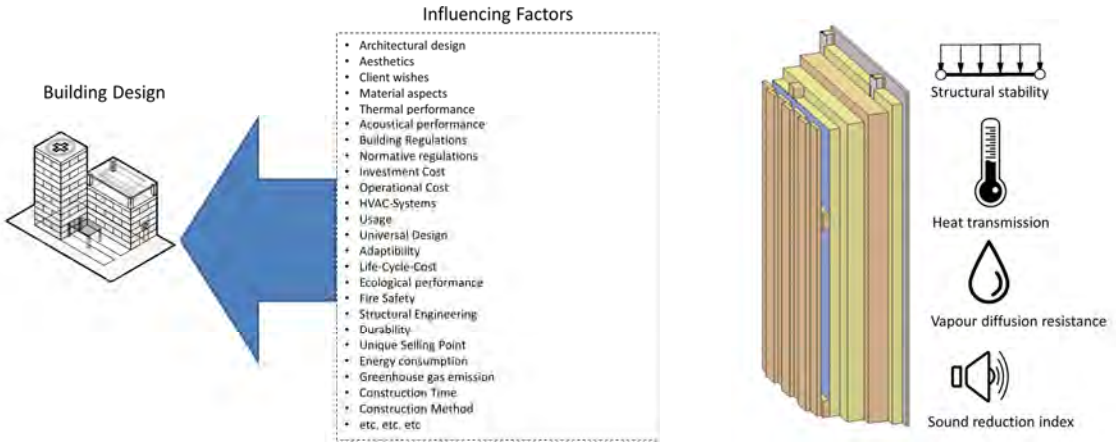

Figure 1: (left) Influencing parameters on building design;
(right) Important aspects that need to be considered in the design of an exterior wall

Formal modelling approaches are commonly used in ICT (information and communication technology) to model real-world situations in a machine-readable and understandable form. They can be deployed to partially automate specific processes, or to form tight rule-based frameworks (grammars) to identify valid solutions for a problem. There have relatively few efforts to adopt these principles (for instance deterministic and non-deterministic finite-state machines, regular languages, or context-free grammars) for the AEC-context. Given the effort regularly invested for routine tasks in the building delivery process (see, for instance [1], for the case of building performance assessment), the potential of such approaches can be considered as significant.

RECENT RESEARCH EFFORTS & NEXT STEPS

Recent projects that underlined the importance of the comprehensive exploration of the possibilities of formal modelling techniques for building-related purposes include the SEMERGY project [2], which targeted the utilization of semantic web technologies for early design evaluation of architectural projects, and – as a follow-up – the BAU_WEB-project [3], which focussed on the efficient provision of building product data in the WWW. In both projects the lack of automation for routine tasks turned out to be a crucial drawback for efficient utilization of time resources. As a response to this circumstance, an initial effort was made toward developing an alphabet and a grammar for building construction assemblies [3]. Further recent efforts include the definition of a set of common use cases. For these, the application of different formal modelling methods could identify the strengths and limitations of the different approaches.

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COMPARISON OF HIGH-PERFORMANCE GRAPH COLORING ALGORITHMS

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INTRODUCTION

The advent of modern many- and multi-core architectures offers the option of utilizing parallel computing to reduce the overall runtime of applications. An attractive option is to decompose a computational task into independent sets, which enables independent parallel processing, i.e., without computational dependencies which potentially limit parallel performance. Such techniques are typically used in, e.g., linear algebra [1], mesh adaptation [2], and community detection [3].
A prominent approach to identify independent sets is to use graph coloring algorithms, in particular so-called distance-1 algorithms [3], which color a graph $G(N,E)$ such that no two neighboring nodes have the same color. Subsequently, the nodes of each color represent an independent set. One drawback of most of these algorithms is the resulting skewness in the population of the independent sets, yielding possibly insufficient workload for the actual parallel processing steps which follow the graph coloring. In this work we compare the results of recently developed parallel distance-1 graph coloring algorithms against well known serial algorithms with respect to the number of colors, population sizes, and performance.

COLORING ALGORITHMS

The *Greedy* algorithm [3, 4] assigns each graph node the smallest permissible color by checking the already assigned colors of the neighboring nodes. An adoption of the *Greedy* algorithm, the *Greedy-LU* algorithm, alleviates the resulting skewness of the distribution of the color populations, by assigning the least used color to the active graph node [3]. In addition to the two serial algorithms, we investigate two shared-memory parallel algorithms: (a) The *Iterative Parallel* algorithm of Çatalyürek et al. [4], which conducts a parallel initial coloring with a subsequent color conflict detection and resolvement step resulting in an unbalanced coloring. (b) The *Scheduled Reverse* algorithm of Lu et al. [3], which generates a balanced coloring using a parallel recoloring approach after an initial *Greedy* coloring.

RESULTS AND DISCUSSION

As first test graph we use a graph representing a tetrahedral mesh of a three-dimensional tri-gate transistor (*Trigate*) with 177 093 nodes, a maximum number of node degree of 50, and an average node degree of 27.31. The second graph is from the University of Florida Sparse Matrix Collection [5], representing the internet topology (*Internet*) obtained from daily traceroutes in 2005 with 1 696 415 nodes, and a maximum and average degree of 23 633 and 8.72, respectively. All benchmarks were performed on a single node of the Vienna Scientific Cluster 3 [6].
In Figure 1 we depict the resulting color populations for the two investigated graphs. As expected, the *Greedy-LU* algorithm produces the best balancing in both cases, but uses the highest number of colors. For the *Internet* graph it requires about 6 times more colors than the unbalanced *Greedy* algorithm. The *Iterative Parallel* algorithm produces similar color populations as the *Greedy* algorithm. The *Scheduled Reverse* algorithm manages to alleviate the skewness resulting from the initial *Greedy*

coloring, but for the *Internet* graph it results in high population differences for higher color classes. In Table 1 we compare the execution times of all investigated algorithms. Our investigation shows that the *Scheduled Reverse* algorithm balances an initial *Greedy* coloring, but at the cost of being nearly two times slower for the *Internet* graph compared to the fastest algorithm (i.e., *Greedy*). Additionally, we show that the *Iterative Parallel* algorithm achieves a speedup of almost 5 for *Trigate* and about 11 for the *Internet* graph. The *Scheduled Reverse* algorithm performs worse in terms of speedup, mostly because it is based on an initial coloring, and an additional serial preparation step, before the actual parallel recoloring can be conducted.

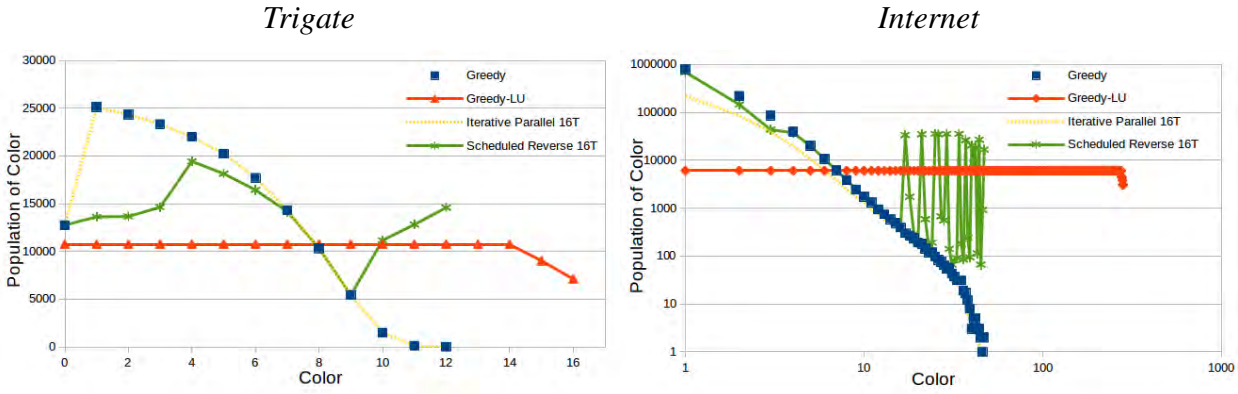

Figure 1: Color population of the two test graphs using 16 threads (16T) for the parallel algorithms.

Graph	*Greedy*	*Greedy-LU*	*It.Par. 1T*	*It.Par. 16T*	*Sched.Rev. 1T*	*Sched.Rev. 16T*
Trigate	0.033	0.096	0.129	0.027	0.062	0.045
Internet	0.462	6.352	5.502	0.492	1.017	0.800

Table 1: Execution times in seconds of the algorithms for the test graphs. For the *Iterative Parallel* (*It.Par.*) and *Scheduled Reverse* (*Sched.Rev.*) algorithms the results obtained with 1 (1T) and 16 threads (16T) are shown.

CONCLUSION

We showed that the *Greedy-LU* algorithm performs best regarding the balancing of the color populations, but can be nearly 14 times slower than the unbalanced *Greedy* algorithm. Adding execution time to the consideration, the *Iterative Parallel* algorithm produces the best results regarding both, parallel scalability and coloring quality.

ACKNOWLEDGMENT

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A GENERAL SCHEMA FOR REPRESENTATION OF MONITORED DATA

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INTRODUCTION

Quantitative monitored information provides the basis for the assessment of building quality with respect to, for instance, indoor environmental conditions and energy performance. In this regard, monitoring-supported verification is a key requirement for reliable building delivery and commissioning processes. Moreover, systematic monitoring, high-resolution, and high quality data can improve the state of knowledge in a wide range of domains in building science, including building integrity and building automation. As such, the relevant professional community is well aware of the importance and benefits of building monitoring. However, currently building monitoring systems appear to operate without a systematic and comprehensive ontology. There have been many efforts in the past to advance interoperability in building data communication with fairly well developed schemes for the constitutive elements of buildings pertaining, for instance, to building fabric. Nevertheless, there is a lack of explicit schemes for representation of sensory information that can be obtained from buildings. To address this issue, the present contribution describes a recently introduced ontology as a general schema for representation of multiple data streams relevant to the building operation. The contribution argues that this ontology is a robust foundation for further developments with respect to applications in building data acquisition, storage, processing, and analysis.

AN ONTOLOGY OF BUILDING-RELATED MONITORED DATA

Whether essentially a unique path to the construction of a schema for building monitoring could be defined or not is questionable. However, identification of basic data categories appears to be a fundamental step towards the construction of a well-formed schema for building monitoring. Based on previous research efforts on this topic [1], [2], [3], [4], we have demonstrated that the following six data categories could provide an effective classification framework to accommodate the empirical data obtained from building monitoring systems. These data categories include, i) inhabitants, ii) indoor environmental conditions, iii) external environmental conditions, iv) control systems and devices, v) equipment, and vi) energy. Figure 1 illustrates these categories along with applicable sub-categories of monitored data.

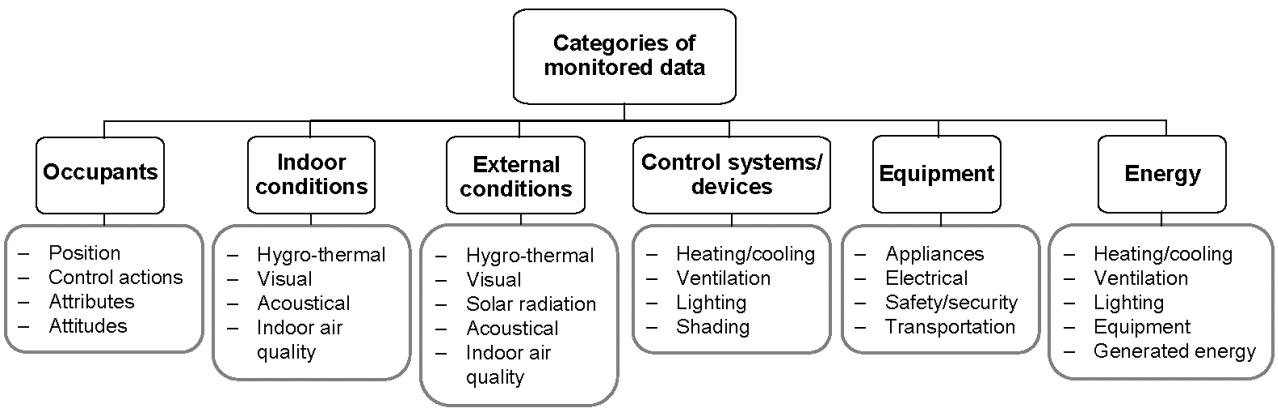

Figure 1: Data categories and sub-categories of monitored variables

Data sources, such as sensors, virtual (simulation-powered) sensors, meters, and human agents generate streams of information in the above six categories. A key requirement of a suitable ontology for the monitored data is a structured and comprehensive definition of the relevant monitored variables. For this purpose, we demonstrated that all monitored data can be captured in terms of the structure shown in the UML (Unified Modelling Language) representation of Figure 2. In each data category and in the respective sub-category, monitored variables are specified in terms of their values, related sources, and actors.

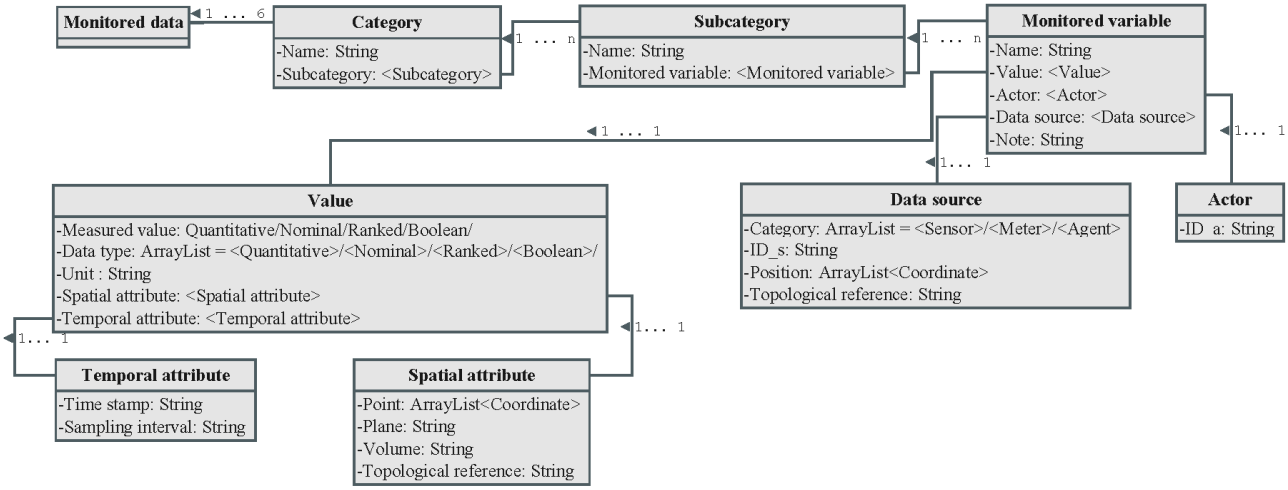

Figure 2: UML-representation of monitored data structure [4]

DISCUSSION AND CONCLUSION

This paper highlighted the lack of richly structured approaches to the collection, storage, sharing, and analyses of monitored data. To address this issue, we introduced an ontology and associated data structure for the representation and incorporation of multiple layers of data. The presented ontology has the potential to contribute to supporting and structuring building data acquisition, storage, and processing in multiple applications, such as building performance simulation, building automation, and building diagnostics.

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SELF-LEARNING OPTICAL MUSIC RECOGNITION

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INTRODUCTION

Music is an essential part of our culture and our cultural heritage. It has been passed on through the centuries primarily in two forms: as aural transmission and in written documents, called music scores (see Figure 1). Reading music scores and playing or singing them requires years of studies, which many people cannot. Optical Music Recognition is the research field, that can help to overcome this problem by automating the decoding of written music into a machine-readable format, which allows for further processing, such as generating an audio file that a user can listen to.

PROBLEM STATEMENT

The idea of Optical Music Recognition (OMR) dates back to the 1960s and 1970s, when the first flat-bed scanners became available [1]. The classical approach is a pipeline of steps, that tries to find the structural elements of music scores, called staff lines, followed by several steps that try to isolate and extract the smaller symbols, called notes and rests, that convey the intended temporal sequence of sounds and rests. After finding those primitives, a semantic reconstruction attempts to recover the relationships between symbols as well as their notational semantics. Finally, the internal representation is exported into formats such as MIDI, which allows to play the music back to the user.

The whole process has often been referred to as Optical Character Recognition (OCR) for music. And although the two share many similarities, OMR presents a significantly harder challenge and has notoriously been underestimated, which resulted in the unsatisfactory result, that there exists no system which is capable of robustly recognizing music scores for any except the most simple cases.

The aim of this research is to improve Optical Music Recognition by breaking with the traditional pipeline and replacing it with a machine-learning approach, that makes use of the recent advances from the field of computer vision by the means of deep learning. Instead of using hand-crafted algorithms, that were tailored to work well on a particular dataset, a machine is trained to recognize music scores by itself from a large dataset, given initial human supervision.

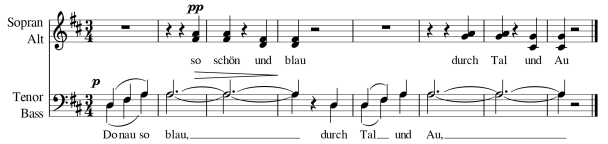

Figure 1: Beginning of Johann Strauss Junior's waltz "An der schönen blauen Donau", arranged for four voices, written in modern music notation.

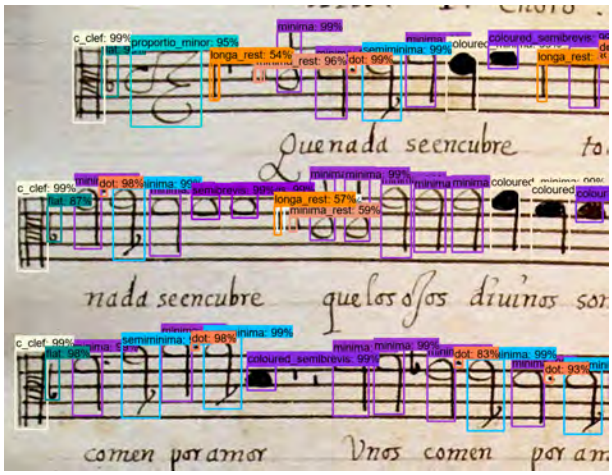

Figure 2: Hand-written music scores, written in mensural notation, with detected symbols, highlighted in boxes with their associated classes on top.

EXPERIMENTS

So far, we conducted several experiments, that tried to answer the following questions: Can a machine learn the concept of "what scores look like" and distinguish music scores from something else? [2] Can a machine learn to distinguish between isolated symbols just by providing enough samples of each class? [3] Can a machine learn to detect all symbols in hand-written music scores? [4]

For each of these questions, a deep convolutional neural network was trained on a large dataset of thousands of examples that were manually annotated by humans. For the last question, various state-of-the-art object detectors such as Faster R-CNN [5] were evaluated and adapted to work well on previously unseen data (see Figure 2). This breakthrough allows the research community to move on to other remaining challenges, such as the semantic reconstruction, which has to deal with a substantial amount of incomplete information and notational subtleties that previously found little attention, because researcher were struggling to solve the preceding steps.

RESULTS AND DISCUSSION

The conducted experiments showed very promising results that were comparable or even better than the performance of humans on the same task. A single neural network for example for capable of distinguishing 79 different classes of symbols with a precision of over 98% and the work on detecting music objects in the scores represents a milestone with detection results of over 80% mean average precision (mAP). For the first time, it is possible to accurately detect the full vocabulary of symbols in hand-written music scores, by just training a computer on a suitable dataset. Nevertheless, there is still plenty of room for improvement, before the machine is capable of reading music scores as good as humans.

CONCLUSION

This work has shown that with recent advances in the field of computer vision and deep learning, it is possible to replace a hand-crafted and often very limited process with an end-to-end trainable neural network, that is capable of learning abstract concepts and solving very specific problems with high accuracy, given the right approach and a sufficient amount of data. We will continue this way and aim towards a system, where the entire process of OMR is end-to-end trainable, allowing the computer to learn and improve by simply providing more data.

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Research Field *INDUSTRY 4.0 – From Smart Factory to Smart City*

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Introduction

The fourth industrial revolution - **so called Industry 4.0 innitiative** – enables resources and energy effcient, flexible and cost effective industrial production in production batch of 1. Industry 4.0 - often regarded as cyber-phisycal production systems (CPPS) is largely enabled through Internet of Things (IoT) – as integration of pyisical devices intelinked with data via internet, thus offering much more than a service of one isolated production unit.

"This is nothing less than a paradigm shift in industry: the **real manufacturing world** is converging with the **digital manufacturing world** to enable organizations to digitally plan and project the entire **lifecycle of products and production facilities**." as Helmuth Ludwig, CEO, Siemens Industry Sector, North America states.

In the context of Industry 4.0 system automation, digital twins, self-optimisation, robotic production, but in front of all big data management and data exchange represent technological challenges and innovation, not only in the field of smart manufacturing, but more over connecting production, transport, energy, resources and people within the larger context of the smart city.

GEOMETRIC COMPUTATION TO SURFACES DESIGN

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INTRODUCTION

As new explorer of building geometric modeling, this is an attempt to control the process chain that links a design idea to its digitalization to be produced. The goal is to get projects of high complexity to take flight thanks to mathematics, informatics and architecture since the link between these three worlds can enable so much more than the conventional architectural drawings. This method of modeling helps to find more freedom in designing, as well as more efficiency and safety in planning.

CONTROL OF THE DIGITALIZATION OF COMPLEX SURFACES

The obtaining of the final digitalization is the result of a chain of actions that have to be controlled from the first moment since one result will be consequence of the previous one. For a better understanding, I will briefly present the steps I followed in each of the phases in a determinated experiment. The main program used throughout all these experiments has been GhPython. It is the Python interpreter component for Grasshopper that allows to execute dynamic scripts.

Approach to the geometric problem: From the beginning we consider the geometric relationships that we want to maintain during the whole process and it is totally necessary to study in depth how they work.

Since I had studied about a mathematical concept called 'cross-ratio', the goal is to create a semi-discrete surface (discrete in one direction and smooth in the other) from a set of biarc curves in which all the vertices of every face are circular. After working on planar faces and consequently discrete surfaces, the choice of biarc curves is because of the structural advantages that we can obtain using circular arcs [1].

Applicability: The study of the maximum number of possibilities in which the procedure can be applied since the more possibilities you have to use it the more useful it will be.

In the presented case, the only restriction is that the initial curve has to be a biarc curve, This is not a problem because the file is ready so that there exists the possibility of transforming any planar or space curve into a biarc curve [2] just defining the number of segments.

Recognition of the parameters: The previous knowledge about the geometric relationships will help to recognize how flexible the results are. In other words, it will help to define the parameters which the initial element will depend on.

To get the successive biarc curves, we are going to use a similar process to the one used in [3] through spheres. The parameters will be the initial point of every biarc curve and the set of angle for every arc in every biarc curve. To work in a easier way the choice of the angle will be illustrated through a NURBS surface formed by NURBS curves that will be represented in a 2-D graphic.

From these transformations we realize that if we apply the null angle we will always get the symmetric biarc curve to which we are computing the transformation. Consequently, every two transformations

with null angle we will get the original curve. We will call 'neutral' to this type of transformations.

In this case there exists a huge variety of possibilities. This is a nice aspect for design because there is no an only possibility.

Control of the final surface: It is the most important step for design since any designer wants the surfaces he is creating to go through a fixed or limited space. If the geometric procedures work in a chain, this control is harder since the change of a parameter in a part of the first curve will affect to the whole surface. In these cases this control has to be done step by step from the beginning.

One of the tests is to check the path of every curve with the control of the position of an endpoint of one arc every two arcs. This is possible with a list of desired points through which we want our curve to pass. To get it, we use the binary search algorithm applied to the values of the angles compared with the 'neutral' case.

Another faster test is established with the use of toggle component in Grasshopper. It is possible to approximate the shape of the surface to the desired one changing the values of the angles and fix them when the results are interesting so that new changes do not induce radical changes.

RESULTS AND DISCUSSION

It is almost impossible to get that the curve passes through the desired points as we presented in the first test because of the geometric limitations but from this method we may get good approximations.

Thanks to the use of toggle component in Grasshopper, there is a way to change the resulting surface in a smooth way and we do not have surprising and undesired results.

CONCLUSION

I have tried to show that there is a way to think of a geometric process to get surfaces and discover the way of controlling the possible parameters to get interesting results.

The next step is the improvement of these methods of controlling to get results closer to the desired ones.

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INTERNET OF THINGS AND THE FUTURE OF LIFE-CYCLE ASSESSMENT IN SMART WORLD

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INTRODUCTION

Robust Life-Cycle Assessment (LCA) requires current and accurate data—that is, inappropriately limited at present, due to the lack of all-inclusive observations and measurements—particularly in developing countries. Moreover, despite advances in (open-source/free) databases and software platforms, procedure of doing a careful and transparent LCA is still remarkably time-taking (viz. it is very difficult to perform rapidly in early stage of design of multipart objects like large buildings or urban districts). Technological breakthroughs namely in Information and Communication Technology (ICT) promise an emergence of the so-called Smart World in which the Internet of Things (IoT) makes it possible to uniquely identify and track everything, anywhere, anytime[11]. It also enables collecting real-time data (e.g. energy and carbon input/outputs) associated with objects via network of sensors, that makes LCA much more precise and automated compared with today's conventional methods[10]. Nevertheless, while about 4 billion people across the world still don't even have internet access[12], how likely is the real Smart World to emerge?

MATERIALS AND METHODS

The so-called Smart Factory is characterized by optimum production management, utilizing advanced ICTs in context-sensitive environment[7]—within its limited system boundary. However, resources, industries, products, users, wastes and emissions are all interconnected and correlated in a complex broad system whose boundary is (at least) as large as the whole Earth. Regarding detailed bills of materials, a factory in one country may use resources, machinery and services from other countries. Thus, real Smart Factories, as aggregation, may arise only when all their up-stream and down-stream effects associated with others also become smart. This will be realized in Smart World. In other words, development of smart environments in local scale highly depends on the improvement of smartness in other environments world-wide, and vice versa.

As Smart City is more complex than Smart Factory, the complexity of Smart World is definitely not less than Smart City. According to the complex innovation dynamics demonstrated in the Triple-Helix model (as a shift from *Mode 2* thesis with trans-disciplinary approach to a bottom-up cultural reconstruction[5]), it is conceivable, that to create a knowledge society in global scale, should improve the interactions between "intellectual capital of *Universities*, *Industry* of wealth creation and their participation in the democratic *Government* of civil society"[5](U-I-G)—all over the world. On the one hand, knowledge, market and learning are in-between-areas (U-I, I-G, and G-U) which express output generated by the three main spheres in *an advanced Triple-Helix network model for Smart Cities performance*[6]. On the other hand, analysis on data about global living conditions shows significant global enhancement in all areas of poverty, literacy, political freedom and education, not only during the last two centuries but also in recent decades[9]. Thus, future development of smart environments in pervasive global scale seems plausible. However, it shouldn't be neglected that extremely-technology-oriented-development of (Smart-) Cities can result in economic polarization, social/spatial fragmentation[4], suburbs and unsustainable urban sprawl[8]. It may also intensify the *brain drain* impact on some developing countries[2]. It's also

worth mentioning that currently many factors that increase emissions and reduce efficiency (at various stages from design to end-of-life) of products, themselves are caused by economic/political problematic decisions, and unsolved social/cultural issues either within countries or between them.

RESULTS AND DISCUSSION

Strengthening the relations between the three spheres of the Triple-Helix model in global scale can gradually generate smart environments around the world and—by paying attention to learning *between* and *across* projects[3]—eventually, Smart World may emerge. In such a situation, taking advantages of pervasive IoT, LCA becomes case-specific, accurate and automated—which could upgrade City Information Model (CIM)[1] to a global version; and when coupled with Augmented Reality (AR), every object will clearly monitor out its desirable/undesirable impacts on natural resources, and consequently, green-washing will be prevented. This leads the world towards the ultimate aim that any LCA is supposed to serve: optimal designs and informed decisions.

CONCLUSION

LCA will reach to its ultimate goals and accuracy only within the context of Smart World. Furthermore, development of ICT/IoT won't lead to emergence of Smart World unless the interrelations of the actors of the Triple-Helix also improve worldwide. Further research on, and development of IoT together with interdisciplinary studies—viz. to integrate it with various fields of engineering, architectonics, urban planning and design—is necessary but not sufficient; in fact international and inter-institutional collaboration between social, cultural, political and economic bodies is also indispensable for identifying and solving problems concerning main agencies of knowledge-based innovation systems in various parts of the world.

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CYCLE TIME OPTIMISATION IN SELF-ORGANISING PRODUCTION LINES WITH HUMAN MACHINE COLLABORATION

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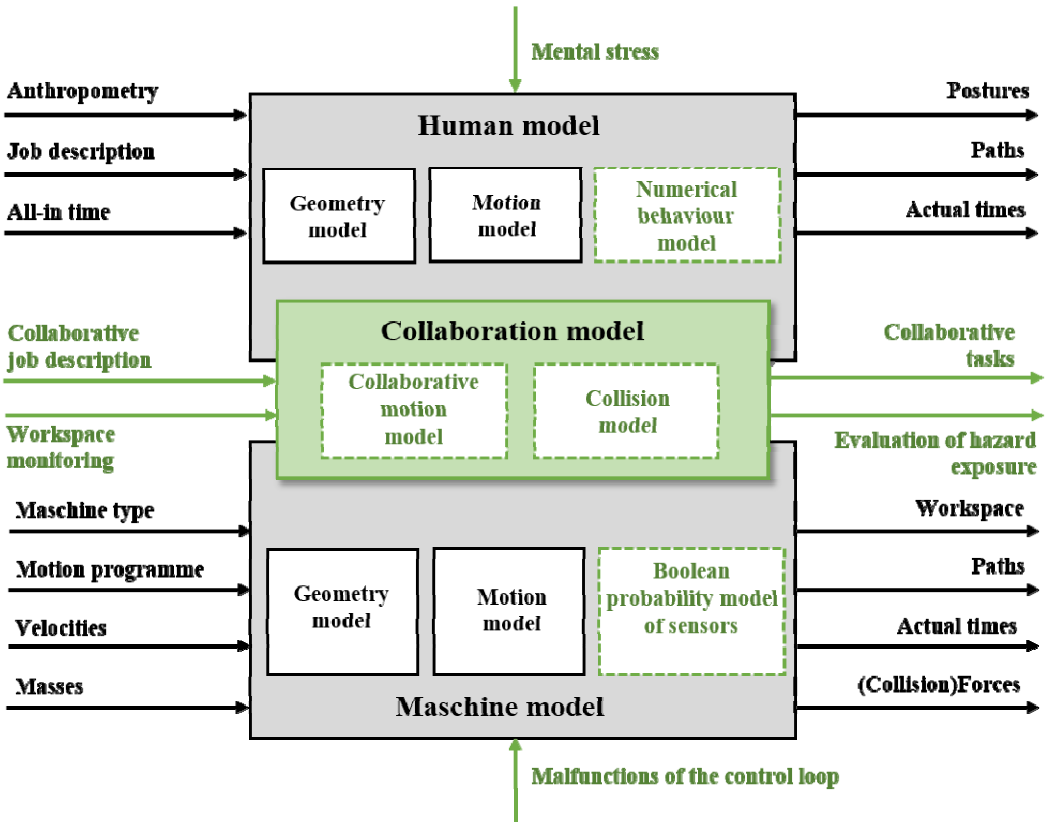
INTRODUCTION

Human machine collaboration refers to humans directly working together with machines on the same workpiece and in the same workspace. In self-organising production lines, humans and machines determine their location of collaboration based on different parameters individually. Thus, cycle time estimation is not trivial, as it depends on order sequence, availability, distance to other collaboration partners, motion parameters and obstacles on the path [1]. In this sense, there is a need for a simulation model, predicting cycle time for this kind of production lines.

MAIN IDEA AND RESEARCH FIELDS

Even though, digital machine and human models already exist to do feasibility, cycle time and ergonomic analyses, they are not used for a consistent planning process in terms of cycle time estimation of collaborative tasks [2]. State-of-the-art simulation tools consider humans and machines separately when it comes to cycle time estimation [3]. One of the main reasons is the different approach regarding motion modelling [4]. As digital human models are also considered as multi-body systems, the high complexity of human motion modelling leads to a lack of performing tasks on moved objects [5]. Furthermore, models mapping malfunctions of the control system or the psychophysiology of humans are not existent and integrated in such consistent process planning tools [6].



Picture 1: Extended model parameters for human machine systems

RESEARCH ACTIVITIES AND RELEVANCE

In this sense, influencing factors of cycle time in collaborative tasks are analyzed [7]. A simulation model is developed, considering not only motion models but also a logical model of the control system including malfunctions as well as a psychophysiological model of collaborative partners. Based on an analysis and classification of collaborative tasks, requirements for modelling human machine collaboration are defined. The collaborative system is then modelled as a simulation-ready hybrid model [8], which is optimised by a multi-criteria optimisation considering production requirements and constraints. Even though, design parameters for collaborative tasks are often in conflict with cycle time and productivity, there is an optimal set of collaborative parameters meeting this trade-off. Based on multi-criteria optimisation an optimal set of physical, psychophysiological and operational costs can be determined for each step of production. The application of the model is shown on different use-cases.

ACKNOWLEDGEMENT

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THE CYBER PHYSICAL ASSEMBLY SYSTEM OF TU WIEN PILOT FACTORY INDUSTRY 4.0

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INTRODUCTION

Cyber Physical Systems (CPS) realize a connection between the physical and the digital world. CPS are based on embedded systems that use sensors to acquire data from the physical environment, process these data by using a microprocessor and act on physical processes via actuators. Different CPS are connected to each other via digital networks (vertically and horizontally) and can access available data and services worldwide. CPS are defined as (technically) unenclosed systems and are characterized by a high degree of networking between physical, social and virtual worlds [1]. The integration of CPS into assembly systems results in so-called Cyber Physical Assembly Systems (CPAS). It is predicted that CPAS will be able to meet the challenges of volatile markets economically and at the same time they will respond ergonomic and age-appropriate work practices [2]. The integration of intelligent communication and information technologies into assembly work systems increases human-system and human-machine interaction significantly. Thereby the direct functional and informational distance between human and work system increases [3]. The scientific literature shows that in work systems of the future, the human workload will increase in a cognitive and physical way mainly. The reasons are primarily due to short-cycle change of work tasks, increasing of complex problem-solving activities and the necessity of flexible staff deployment [4].

Figure 1: Collaborative robot assistance systems

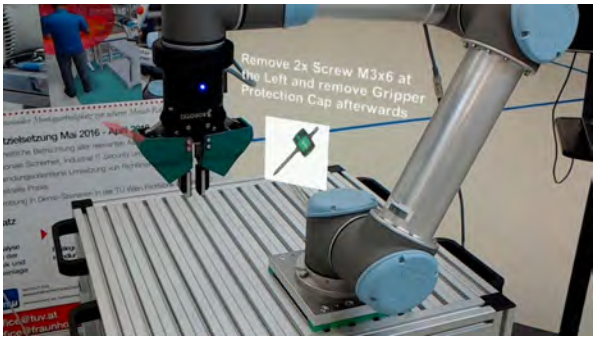

Figure 2: Digital assistance systems (Augmented Reality)

MAIN IDEA AND RESEARCH FIELDS

Based on the concept of a CPAS, in the project "TU Wien Pilot Factory Industry 4.0" a corresponding assembly system is currently developed for in-depth research and industry-oriented demonstration purposes. The assembly system is based on four separate mobile assembly stations, along different variants of a 3D printer are assembled, focusing batch size 1 – according to the principle of a mixed model assembly system (MMAS). Auto-ID technologies such as passive and active RFID (radio-frequency identification systems) enable a decentralized coordination between the adjacent logistics area and material transport. In this complex assembly system, the operator is supported on the one hand by cooperative and collaborative robotic systems and on the other hand by digital assistance systems. The assistance systems are adaptive. The functions of the assistance systems are adaptable to order load-specific requirements and individual human needs. Therefore, a “Human Motion Capture“ system and various local positioning sensors record ergonomic stress situations of the operator. The gained information are also used to analyze synergy effects between

the productivity of the assembly work system and ergonomic situation of the operator. In addition the gained information are used for the objective of incorporating gained knowledge into optimized production planning and control algorithms [5].

RESEARCH ACTIVITIES AND RELEVANZE

The specific research and development activities, which are pursued in the context of CPS are focused on methods to plan and to evaluate assistance systems, referencing the use of (a) digital assistance systems and the use of (b) technical assistance systems, like human-robot collaboration systems in assembly environments [6] [7].

Digital assistance systems support the operator in a cognitive way by carrying out his activities and guarantee a sustainable and productive interaction between the operator and the information system. Furthermore, the operator is supported by digital assistance systems by an adequate interaction with auxiliary and operating resources of the peripheral assembly equipment that interacts with the human situation – e.g. intelligent screw systems [8]. Beyond digital assistance systems, technical assistance systems address operator support in regard to physically stress situations [9]. Sensitive and collaborative robot assistance systems provide context-sensitive and situational support for the workers. Digital and technical assistance enable ergonomic, age-appropriate and productive work systems [6]. In addition to business-oriented and human-oriented planning and evaluation methods, within the TU Vienna Pilot Factory Industry 4.0 Cyber Physical Assembly System we also research and develop integrative safety and security concepts for these new forms of assistance systems in industrial assembly environments.

ACKNOWLEDGEMENT

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CALIBRATION OF A ROBOT ARM USING LASER TRACKER MEASUREMENTS AND ARTIFICIAL NEURAL NETWORKS

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INTRODUCTION

Robot arms offer a high repeatability, which is for most tasks e.g. pick and place sufficient. However, if a precise absolute pose of the robot arm end-effector is questioned, a calibration is inevitable. The kinematics of such robot arm is well understood, however considering its mass or forces acting on it, can lead to a complex system. Generally, if the description of a system cannot be established on basis of physical models due to its complexity, Artificial Neural Networks (ANN) can be used. In this contribution an ANN is built calibrating the zero positions of the encoder. However, the aim is to include stochastics and physical information into the ANN. The estimation of the ANN in the extended Kalman Filter (EKF) enables the integration of stochastic information in the chosen approach.

EXPERIMENTS

The test object is an industrial 6-axis robot arm. A kinematic system description of the robot arm includes the encoder values and the arm lengths. In order to calibrate the robot arm, the absolute end-effector positions are measured by a laser tracker and the position error is used as an output in the ANN. To keep complexity of the ANN low and due to the reason that the zero position of the encoders is the main error source of absolute position errors of such a robot arm [1], the ANN input is only based on the encoder values. Consequently, the robot arm system consists of six encoder values as inputs and three position errors as outputs dx, dy, dz. The generated data set bases on 800 robot arm poses distributed in the working field. 600 positions are used for the training and 200 to test the generalization capability of the generated ANN, see Figure 1.

The weights of the ANN are estimated in the Extended Kalman Filter (EKF), which has been proposed by Singhal and Wu[2]. Thereby, the ANN serves as the observation equation and the system equation corresponds to a static model. The method consisting of ANN and EKF is compared to the standard ANN computation on basis of Levenberg-Marquardt (LM). The two methods are equal under specific assumptions. However, the estimation in the EKF offers some features[3].

The model selection task of determining the number of weights/knots in the hidden layer of the ANN has been accomplished by cross-validation.

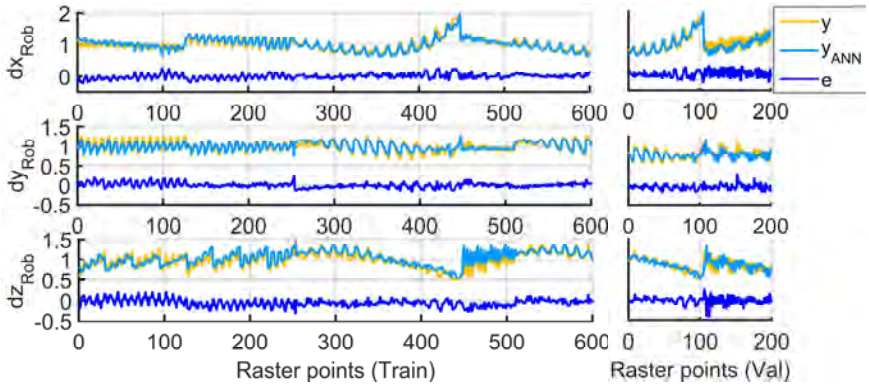

Figure 1: Position deviations in mm
(for a better visualisation y and y_{ANN} are shifted by +1)

RESULTS

An advantage of the proposed method has already been figured out in the model selection task, which needs 30 weights less in the hidden layer than the standard approach (LM). If less weights need to be determined, the number of observed robot arm poses can be reduced significantly. In Figure 1 the result with the best generalization capability is presented, which has been reached by only updating the covariance matrix of the weights. Furthermore, the updating step in the EKF leads to a faster convergence. Consequently, the chosen method offers some advantages.

CONCLUSION

This is a first approach to describe a kinematic robot arm system by ANNs. The stochastic information of the observed absolute position deviations is considered in the calibration of the encoder zero positions. In future the additional benefit of the EKF approach shall be figured out in more detail. The aim is to integrate knowledge of a system as e.g. a mechanical model in the presented approach.

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ELEONAS ATHENS - INDUSTRY 4.0 CONCEPT

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INTRODUCTION

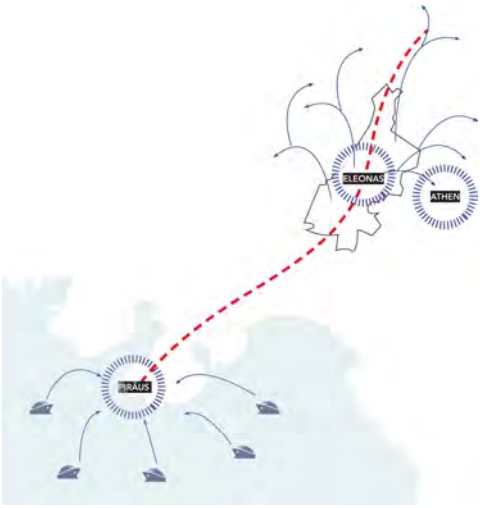
Within the context of an urban planning project, the focus refers to figure out if high-tech industrial revolution can take place in backwarded areas as well. Therefore, we developed a scenario in order to boost industrial activity and to get a forerunner in modern industries. To be more precise, the project is addressed to the district of Eleonas located next to the city centre of Athens which reflects to such an undeveloped area. Not even general tasks of urban planning have to be considered, as well five different political municipalities do have their sphere of influence in Eleonas which made it more complex.

EXPERIMENTS / FUNDAMENTAL OF THE PROBLEM / EXAMINATIONS

Giving an overview about the area/situation: A kind of industrial activity has always been taken place in Eleonas. Starting with agriculture in producing olive oil at the beginning of the 20th century, industrial productivity continued in small scaled businesses and turned into big scaled factories and logistic facilities. Due to major migration streams and political disagreements during the last decades, industrial development was always been left by itself. That's why there is uncontrolled growth in Eleonas nowadays.

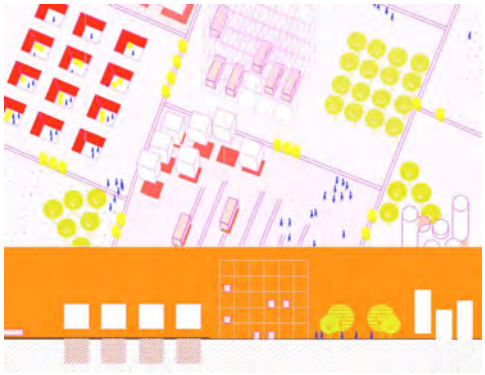
© Veličović: Eleonas - poor developed area

Why rethinking Eleonas would be a good choice for initiating industrial revolution is simply explained in three points: First, as mentioned above, the district is located close to the city centre which means there are a lot of advantages urban cities do have these days, including suburban mobility, infrastructure, education and healthcare system. Second, economic situation still suffers from the crisis of 2008. Situation cannot get worse! Being aware that might be a provocative approach, we believe a restart could recover the chance of high end industrialization. Third, the harbour of Piraeus is part of the so called *silkroad* which is a major infrastructure project initiated by the Chinese government. Piraeus should work as a bridgehead of this road. Therefore, the container terminal has been leased by COSOC, a major Chinese shipping company. Since 2009 they have already started to enlarge the terminal. The proposal is to reactivate and to improve industrial productivity in order to get a forerunner in modern high tech industries. Enable to set in motion the next generation of industry and to create a logistic and industry hub, two aspects seem worth to be discussed: First, the connection to the container



© Hainzl: Harbour Connection

terminal of Piraeus has to be extended in order to transport goods quickly and non-stop to the city centre. Implementing fast trains, magnetic railways or a hyperloop system may be suitable considerations. Eleonas should work as an integrate in a chain of distribution. From there, goods which are mainly coming from Asia, should be spread to Europe and finally to the consumers. This measure corresponds to the so called *silkroad* which is mentioned above. Second, we have to rearrange ownership and to reorganize the present building structure in order to assemble different skills/qualities of the existing industry and to gain public space. The latter allows to realize necessary infrastructure projects as well, e.g. streets and mobility concepts, electricity, extension of fibre cable for going global. Creative diversity and industrial productivity should be visible to the public in so called store and smart factories while production on demand is aimed to be state of the art. We intend to create an area where different players of different fields do have the opportunity to combine their skills. Permanent building structure will be removed by or changed into flexible/temporary units according to requirements of the producers/participants. Co-working spaces and creative labs enable interactive networking processes and stimulate productivity. Those flexible working units should provide all necessary infrastructure and attract skilled people from outside to settle their businesses in Eleonas.



© Hainzl: Vision

Finally, all these measures should lead into a highly modern framework of an digitalized and autonomous working industry. Supported by good educational facilities like universities and research centres, Eleonas could become an attractive place to work amid of good infrastructure and open spaces. Well educated students and qualified employees may achieve pioneering work in high tech industry, mobility or sustainable energy supply. Once, industrial revolution has started, it should end up in a completely autonomous working industrial zone which is pioneering in many disciplines. Giving a prospect to the future, it might be not excluded industrial revolution will arise to the next generation 'Industry 5.0'!

RESULTS

Finally, it is necessary to mention that the project has not come to an end yet. It should be clear as well that it is a kind of prototyping which means that some visions of the output may be followed by a more speculative approach than scientific proof. That's why it might be hard to say anything about the results and in which way they could be transformed into reality. But, according to our current steps of working, two statements can be made for sure; the complexity is caused by many different parties which are involved, and 'Industry 4.0' is not the end of industrial revolution.

CONCLUSION

Initiating industrial revolution based in underdeveloped areas (like Eleonas) is not a question of single players, it is based on skills, qualities and responsibility and how they can be bundled in order to realize sustainable industrial development. Urban planning, law, politics and technical improvement enclose the frame of realization. It is needed to think in big scales when intending to change existing systems and habits of society. And that's what our topic is about. This can only be converted into reality by disregarding individual intentions and to concentrate on higher goals. Our next steps will be to find out in which way participating parties are influencing such a big scaled process of development and how to be involved in order to achieve their own goals.

INDUSTRIALIZATION OF THE PROCESSES IN THE KITCHEN

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INTRODUCTION

The Cloud as an idea has existed for more than twenty-five years.[1] It has been the main tool of information processing and exchange in the business world. More and more, however, it has grown out of the business sector and have entered the personal sphere. It is the crucial part of Industry 4.0, serving as the primary connection between the production and end customer.

As technology evolves, Industry 4.0 is becoming more and more personalized, finding its way into areas where it was once impossible to even imagine it. The kitchen is one such place, where Industry 4.0 can play an important role in the future in areas such as waste reduction, reduction of the wastefulness of resources, availability of bioorganic produce and its freshness, and more, by equalizing food production, packaging and distribution with the consumer purchase and preparation.

Such equalization could be achieved through the use of the Cloud.

EXPERIMENTS / FUNDAMENTAL OF THE PROBLEM / EXAMINATIONS

The project Kitchen was developed by Christoph Luchsinger and his team as part of the Rijeka Open City Concept at the Institute of Urban Design and Landscape Architecture at Faculty of Architecture and Planning in Vienna for the European Capital of Culture 2020 based on the general concept of the Kitchen.[2] The Kitchen contains many different aspects of the city of Rijeka, such as the history, way of life, food and culture of its inhabitants. As part of this section of the project, the idea for the industrialization of the processes in the kitchen was developed.

The idea is for a service that would allow for the end user to identify which ingredients they would need for their meal and their quantity, and on the other end, contain information regarding the availability of those ingredients within or without the city limits at that exact moment. The system would offer rapid delivery of fresh ingredients to the end user's location of choice, whereby those ingredients would not be pre-processed in any way, bot would come straight from the source at that moment (e.g. fruits picked from their trees, rather than harvested, processed and packaged days previously). This would not only allow for a better regulation of production in direct response to the demand, thereby avoiding unnecessary overproduction and wastefulness of unneeded produce, but also boost urban farming with the goal of the reduction of overexploitation of the rural natural resources.

The second concept that the service would offer would be for the purpose of connecting people within the community by promoting the idea of 'kitchen sharing': the user would decide whether to order only the ingredients, but also the service of either 'kitchen renting', where individual users would offer their kitchen space for use, or meal preparation, whereby established cooking services at predetermined locations would receive the recipe and the food, and prepare it for the user. Two main types of end-users would be easily assigned to these categories: the city residents would be most likely to use the food ordering, at most the kitchen renting service with their acquaintances from their community, while tourists would be far more likely to use the cooking services, or

perhaps kitchen sharing if they wish to meet the locals and familiarize themselves with the customs and culture of the city.

RESULTS AND CONCLUSION

The expected result of this study would be app development and identification of necessary resources (e.g. locations for the cooking services, product suppliers, transportation systems, etc), together with a guidebook for the local government with respect to legal food regulations as they might pertain to this system.

Rijeka is a perfect city for the experimental implementation of such a system, given its recent attempts at citywide changes with the aim of pulling out of stagnancy, and connecting this system to an already established project such as the Rijeka Open City Concept would allow for a potentially easier implementation and integration within a wider concept of promoting the culture and customs of the area.

Finally, a system of this kind would contribute towards the streamlining of a previously top-down process beginning with food production and ending with meal preparation, by equalizing all the individual steps and allowing for direct communication different levels of the process.

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INTERFACING ARCHITECTURAL DESIGN AND INDUSTRY 4.0 CONCEPTS: A CASE STUDY

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INTRODUCTION

This contribution describes a TU Wien teaching and research activity pertaining to the relationship between architectural design and Industry 4.0 concepts (such as intertwining ICT and production processes, digital modelling for prefabrication, etc.). Thereby, interdisciplinary student teams from the graduate programs Architecture and Building Science and Technology were given the task to develop and evaluate the performance of new façade solutions for the envelope retrofit of an existing building in Vienna. This building – situated in a prominent location at the Danube channel – can be considered to be a representative of reinforced concrete skeleton buildings of the 1950 – 1970 period. Buildings of this period, influenced in part by the rationalist paradigm, often provide good interior qualities. For instance, they display good daylight availability, given large window areas. Likewise, functional solutions benefit from simple configurations. However, other properties, such as the thermal performance of the original envelope, do not meet today's standards. Given the strict rectangular and repetitive forms of both ground plan and envelope, such buildings appear to be good candidates for the application of industry 4.0 concepts for retrofit planning, such as parametric design, rapid prototyping and individualized prefabrication of façade elements. The majority of design concepts developed by the students participating in the course adopted these ideas. In this contribution, we illustrate some of the retrofit concepts developed in the framework of this design course and discuss their connection to industry 4.0 principles.

THE CASE STUDY BUILDING

The case study building was designed by the architects Wörle and Doskar [1] and was completed in 1961. It is situated in Schwedenplatz within the city centre of Vienna and facing the Danube channel. Figure 1 shows the building (as of 2017) within its urban surroundings. The building possesses three street facades. It and features a ground floor area with commercial functions, plus nine upper floors with mixed office and residential usage.

Figure 1: Case Study building (taken from google earth –

RETROFIT IDEAS

Six different retrofit concepts were conceptualized in the first step of the course and subsequently subjected to an intensive and iterative review, evaluation, and development process. Thereby, different aspects were taken into consideration, including the aesthetic implications of the interventions, their compliance with building codes and standards, their general usability, construction time, and cost, as well as the thermal, visual and acoustical performance of the façade and the overall building. Some of the concepts integrated original approached, such as adding a moveable layer in front of the existing façade, or attaching a new façade in front of the existing one, prior to demolishing the older envelope layer (thus protecting the interior of the building from the outside elements in the course of building retrofit). Figure 2 illustrates these six concepts.

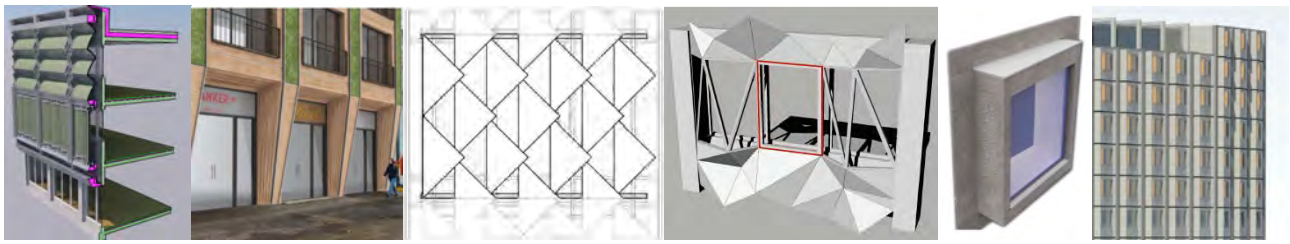

Figure 2: Six different concepts toward façade retrofit for the building at Schwedenplatz, Vienna

INDUSTRY 4.0 ASPECTS IN THE DIFFERENT RETROFIT CONCEPTS

The students were asked not only to provide the design of the new façade, but also consider aspects of building construction, building performance, and construction time. The latter is of crucial importance at the specific location of the selected building and its spatial constraints. Thus, all of the concepts employed factory prefabrication and rapid on-site-mounting. To achieve this, multiple issues had to be considered, including the module sizes (for transport), the mounting process, the interfaces of the modules to each other and the existing construction, as well as the requirements pertaining to the craftspeople involved in the mounting process. Some of the groups employed parametric concepts in their design. Toward this end, parameters such as shading properties and insulation were used as input data for digital and generative design processes. The resulting design vocabulary was then used to configure individual modules, adapted to the requirements of the target mounting position in the façade. Subsequently, the prefabrication process and the transport and mounting procedure were modelled. This approach allowed individualizing the façade modules without giving up the advantages of prefabrication.

RESULTS & CONCLUSION

All six façade designs were repeatedly subjected to a multidisciplinary review by different domain experts to identify strengths and potential weaknesses. Generally speaking, in all proposals, a theoretical decrease of the on-site construction time on site could be achieved as compared to traditional façade retrofit processes. It can be concluded that such design and construction processes, once established on a broad basis, has the potential to fundamentally change approaches to building and retrofit planning and corresponding construction processes. To validate the proposed approach, it would be of course necessary to apply it in a real world façade retrofit project involving building planning and construction professionals.

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WAFERMAP PATTERNS CLUSTERING VIA VARIATIONAL AUTOENCODERS

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INTRODUCTION

"Industry 4.0" has confronted with new challenges to be able to compete in the increasing global markets in the past couple of years. The industries decided to adapt their manufacturing processes to new paradigms such as automated root cause analysis and decision making in the semiconductor manufacturing. Defect detection from given sensory data is one major goal of their contribution. Defects are exhibited in typical shapes such as rings, spots, repetitive patters or scratches. Several methods has been proposed to recognize these patterns based on traditional image processing [1,2]. There also have been proposed methods on supervised training of mixture models [3], neural networks [4], or support-vector machines [5]. All these methods require a human expert to manually label the data of training dataset. By using unsupervised approaches the intervention of human experts is eliminated and the hidden dependencies between various kinds of wafer defects are detected automatically which enables detection of patterns that were unknown or overlooked before. Our goal is to provide an unsupervised method for clustering the wafermap patterns using variational autoencoder. Our algorithm is proceed in three steps: (1) pre-processing of the raw wafer dataset using computer vision techniques, (2) extracting features by training variational autoencoder on the cleaned data, and (3) clustering latent features and group the wafers based on a distance measure using k-means clustering.

PRE-PROCESSING PHASE

The wafer dataset contains some irregular shapes of wafermaps for missing values (or holes) within the wafer area. We binarize the wafer by replacing all present values with 1 and all missing values with 0. We then close the small holes by mathematical morphology approach. All binary morphological operations are the result of combining two morphological operators–erosion and dilation. The former is sufficient for closing the holes in the binary clipping mask. Although random measurement errors caused by physical limitations of manufacturing device lower the quality of recorded data, they are usually within certain range and do not cause major problems when building a predictive model. However, occasional large inaccuracies or malfunctions in measurement process can introduce errors called outliers. The mean and standard deviation, used to to characterize normal distribution, are especially susceptible to perturbations caused by outliers. On the other hand, median is resistant to gross errors in up to 50% of the samples. Our method uses modified Z-score to detect the outliers.

FEATURE EXTRACTION PHASE

The dataset obtained by pre-processing can be seen as a random discrete variable X consisting of d individual samples $x_1, \ldots, x_d$. In order to overcome the course of dimensionality for the classification task, we extract only the most salient features $z_1, \ldots, z_d$ represented by normally distributed variable Z. The approach used for this task is based on auto- encoding variational Bayes.

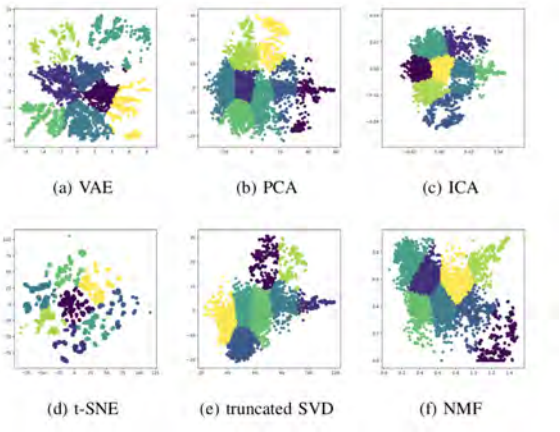

Figure 1: Wafer dataset projected into two dimensional latent feature space and clustered with k-means into 8 clusters. Different feature extraction methods have been used: (a) Variational Autoencoder; (b) Principal Component Analysis; (c) Independent Component Analysis; (d) t-Distributed Stochastic Neighbor Embedding; (e) Truncated Singular-value Decomposition; (f) Non-Negative Matrix Factorization.

CLUSTERING PHASE

Clustering groups set of objects together based on a similarity between them. We typically recognize two types of clustering -hierarchical clustering which groups the set of objects into a hierarchical tree and partitioning clustering which groups the set of objects into a disjoint subsets, s.t. each object is exactly in one subset. Given a set of n latent features $(x_1, x_2, \ldots, x_n)$, we cluster them with k-means into a disjoint clusters $C_1, C_2, \ldots, C_k$. The objective of this algorithm is to optimize squared Euclidean distance between the latent feature x and the centroid μ_i of the cluster C_i till convergence.

EXPERIMENTS

In order to evaluate the performance of the algorithm presented in this paper, we have compared the variational autoencoder approach with other commonly used decomposition methods. The same pre-processing and clustering algorithm have been used in with all tested methods. Detected clusters for two dimensional latent space can be seen in Figure 1.

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LOSS- AND DISTORTION-FREE TRANSLATION BETWEEN DATA MODELS IN OPEN BIM

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INTRODUCTION

Building Information Modelling (BIM) was developed as a method of information exchange in the Architecture, Engineering and Construction (AEC) and Facility Management (FM) industries. In its simplest form it is a data model that couples geometry with non-geometric information (e.g. material properties of a wall)[1]. However, BIM can also be regarded as a method of interaction between all stakeholders in the above mentioned industries, in which case it aims at not just information exchange but at providing feedback and enhancing real-time communication (e.g. collision detection between the ducts in a ventilation system and the pipes in a water supply system and automatic generation of wall penetrations for both). The complex interactions within the data model of BIM are software-dependent and not standardized. Some data models behind BIM – in particular the Industry Foundation Classes (IFC)[2] standard for Open BIM – are publicly available[2] and used as a data exchange standard between applications. The main challenge with the implementation of IFC is the loss and / or distortion of the information during the exchange process. One of the major reasons for it are translation problems between the internal data model of the application and the IFC data model, which in its IFC4 version contains more than 600 type and entity definitions. This work aims at defining a loss- and distortion-free translation method between data models as well as techniques for user control and verification of the translation results.

EXPERIMENTS / FUNDAMENTAL OF THE PROBLEM / EXAMINATIONS

There are two main challenges in designing a loss- and distortion-free translation between two data models – the lack of precision in the natural language and discrepancies in the level of detail between data models.

Behind each data model there is a taxonomy based on a natural language. For example, the term “local axes” can hold different meaning depending on the domain – for an architect it could be the local coordinate system for drawing a wall, whereas for the structural engineer it could be the load bearing axes. This can result in information distortion - the wall changing its position after translation from the architectural to the structural domain, because a local coordinate system can be placed anywhere, even outside of the object, but the structural axes are generally, but not always, placed symmetrically within the object. This challenge can be met by providing user control of the translation or by replacing the natural language term by a data model which encodes the dependencies described above in a graph-like structure.

This leads us directly to the second challenge – the level of detail. Each application requires a level of detail (or information granularity) in its data model that is adequate to its function. For a software in the architectural domain it is sufficient to represent a wall construction as a sequence of material layers. A software in the building physics domain, however, may require further subdivision of the material layers if they are inhomogeneous or if, for example, a simulation of the heat flux within the

wall is to be performed. This becomes problematic if the translation path leads from the more detailed model (building physics) to the less detailed (architecture) to the more detailed model (building physics) again. To prevent information loss we need a data model of the translation process itself, which defines transition rules between, for example, the grid size of the battens layer of a roof construction in the architectural domain and the individual geometry and placement of each batten in the building physics domain.

RESULTS AND DISCUSSION

The translation methods described above present their own challenges – mainly an increased complexity in all data models involved. A major example of that is the IFC data model which incorporates structures for all domains in the AEC and FM industries. As of version IFC4 it no longer contains the parameters of its own data model (e.g. the U-value for a wall construction), but instead requires a dedicated parameter data base that can be queried by elements of the data model (e.g. the wall construction can look for its U-value). This development shows that the complexity of a data model can be reduced by separating it into groups or layers depending on its level of detail and specificity.

The methods of Model Driven Engineering (MDE)[3] and Multi-Level Modelling (MLM)[4] are particularly well suited to this challenge. They enable a formally defined separation of a data model into an arbitrary number of data model layers, in which each element serves as the type for multiple elements in the layer below[5]. In this way it defines the type and format of information they are allowed to carry and provides automatic verification of those elements in a translation context.

CONCLUSION

Reduction of complexity and control of the quality of information flow are easier to achieve in a highly structured environment (e.g. a multi-layered data model with few elements per layer) as opposed to a flat environment (a single-layered data model containing all elements).

The aim of this work is to provide guidelines for discovering imprecise definitions in data exchange standards and replacing them with data models, to develop algorithms for separation of large and complex data models into multiple data model layers and for translating between such multi-layered data models. The IFC standard, Drawing eXchange Format (DXF)[6] and a simple data model developed in a previous project, Simultan[7], will be used as case studies.

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MODELLING METHOD FOR THE OPTIMAL OPERATION OF SENSIBLE THERMAL ENERGY STORAGES

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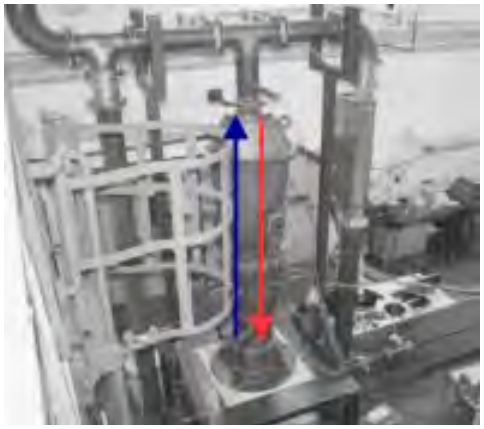
INTRODUCTION

To reach the EU's climate targets, an important topic is energy efficiency in energy-intensive industry and integration of renewable energy using energy storages. In Europe industrial processes have a share of 25.3% of the total energy consumption[1], therefore improvements in this sector have a huge impact. In this regard, a smart energy system approach[2] is promising, interconnecting industry with electricity, heat and gas networks. This allows a better integration of renewable and higher overall efficiencies due to higher flexibility. Though, these interconnections create a complex system, which needs to be operated in an optimal way. In such an energy system, there are lots of different generating units, storage units, interconnections, etc. The problem of optimal operation of these units is referred to as unit commitment (UC) problem[3], which can be solved, e.g. with mixed integer linear programming (MILP), a mathematical optimisation method. In this contribution, a novel method for optimal operation of a sensible thermal storage is presented.[4]

METHODOLOGY

The fixed bed regenerator (Picture 1) is a sensible thermal energy storage, meaning that the storage is charged by increasing the temperature of the storage medium and discharged by decreasing its temperature. The storage behaviour has nonlinearities, as most real physical system have, but MILP allows only linear terms, therefore the nonlinearities need to be approximated appropriately. Note that there are as well nonlinear optimization methods, but these could find just a local and not the global optimum of the optimisation problem or they are too inefficient to solve the problem in reasonable time. The realistic dynamic behaviour of the storage is depicted in Picture 2. It can be seen, that the charging/discharging power is not only dependent on the storage fill level, but also on the fill level at the beginning of the current phase (charging or discharging). Storages in MILP-UC problems are mostly modelled with a fixed maximum charging and discharging power (Q). Such a simple storage model (Model A) can be described with the following equations.

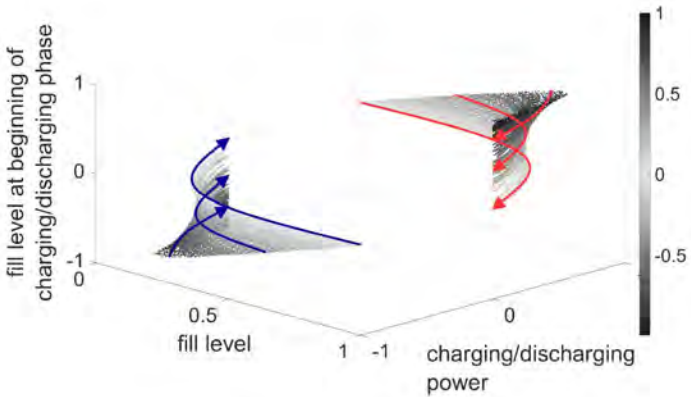


Picture 1: Fixed bed regenerator (Sensible thermal energy storage) [4]

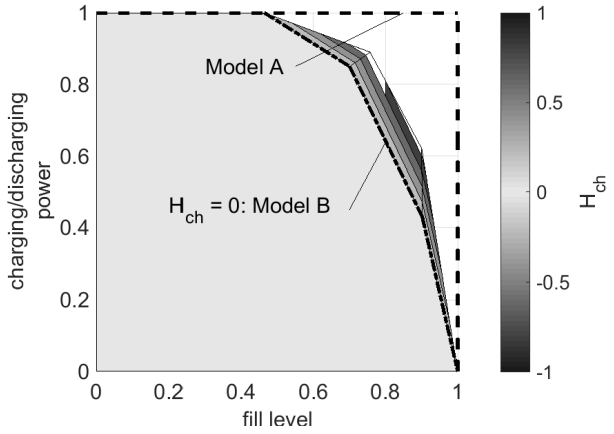
$$S_{t+1} = S_t + (\dot{Q}_{ch,t} - \dot{Q}_{dis,t}) \cdot \Delta t, \quad 0 \le S_t \le S_{max}$$

$$\dot{Q}_{ch,t} \le \dot{Q}_{ch,max}, \quad \dot{Q}_{dis,t} \le \dot{Q}_{dis,max}$$

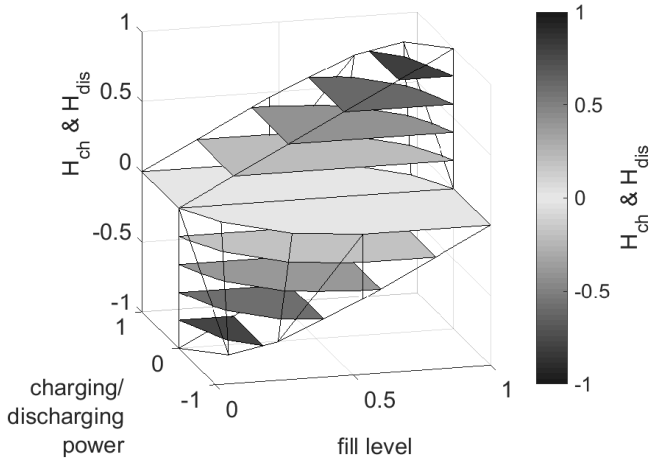
According to Picture 2, the maximum charging or discharging power is not fixed. To this end, the model can be extended as follows (Model B).



Picture 2: Dynamic operation of the fixed bed regenerator[4]



Picture 3: Model A, B and C (bottom view of charging part) [4]



Picture 4: Model C[4]

$$\dot{Q}_{ch,t} \leq a + b \cdot S_t \quad , \quad \dot{Q}_{dis,t} \leq a + b \cdot (S_{max} - S_t)$$

Picture 3 shows the maximum power for Model A, which is constant, for Model B, which is just dependent on the fill level (*S*). Model C is a further extension of Model B with more complex constraints, where additionally the fill level at the beginning of the current phase is considered (H). Model C is illustrated in Picture 4. Picture 3 shows the bottom view of the charging part of Model C. Compared with Picture 2, Model C is the most precise of the three Models.

RESULTS AND DISCUSSION

The presented models were compared with a test case, which consists of a combined heat and power (CHP) unit and the presented storage. A predefined heat load has to be satisfied, the fuel costs for the CHP unit are constant, and the electricity prices are taken from historic spot market. Model A has the worst feasibility and objective value, Model B is a very reliable and feasible representation, but cannot exploit the storage capabilities to its fullest. Model C can represent the storage most accurate, but needs higher computational effort.

CONCLUSION

Compared to the simple formulation of energy storages, the presented extended MILP model C for sensible thermal energy storages is able to better exploit the storage flexibility and decrease prediction errors that would lead to further efficiency reductions. With this more precise storage modelling, the efficiency of the overall energy systems will be increased. This modelling approach, as well as other studies of the authors[5], can be integrated in state of the art MILP-UC formulations. Currently the authors develop an efficient MILP formulation for multiple identical generating units and investigate the impact of different time step sizes on the MILP-UC problem.

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MULTI-SCENARIO SIMULATION AND EXERGY ANALYSIS OF A DISTRICT HEATING NETWORK FOR A CASE STUDY IN THE CITY OF VIENNA

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INTRODUCTION

District heating networks are systems for the transport and distribution of thermal energy, responding efficiently to consumers´ needs. They are an important part to take into account inside urban energy facilities.

Between all possible methods and procedures to analyse the urban energy strategy, a proper hydraulic simulation able to calculate automatically mass, energy and exergy balances reveals itself as a fundamental previous step before beginning any project or design related to this field. Likewise, calculated energy and exergy efficiencies gives advice to urban planners about which is the best option between different considered scenarios, like changes in installations or operation conditions.

PROBLEM DESCRIPTION AND METHODOLOGY

In order to answer these questions, one of the districts of the city of Vienna has been taken as a case study, consisting of 21 residential buildings with different characteristics, all of them connected to the local district heating network, with its corresponding substation that exchanges heat with the primary network.

Each simulation is constructed from each of the hypotheses proposed at the beginning of the study. A hypothesis is traslated into a scenario, that is, a new configuration and/or operational conditions under which the district heating network must operate. For example; verifying the performance after a 30% reduction of the feed temperature.

8 scenarios were defined, based on the following main considerations:

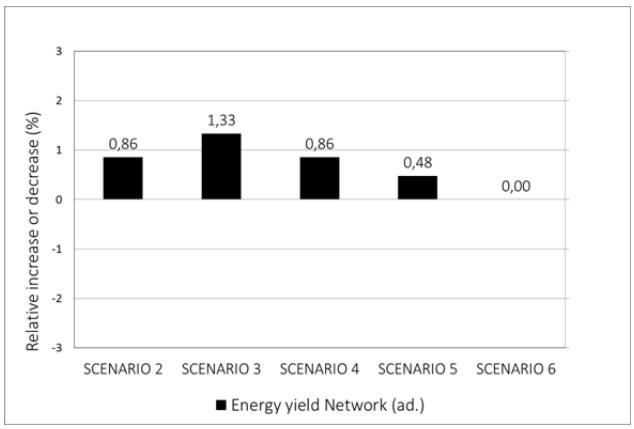
- Actual situation
- Replacement of current heating systems (from radiators to heated floors), with the corresponding buildings´ refurbishment.
- Reduction of system´s temperature, considering Low Temperature District Heating (LTDHN) knowledge [1].
- Introduction of heat pumps in combination with district heating networks, allowing a higher use of electricity in the system [2].

RESULTS AND DISCUSSION

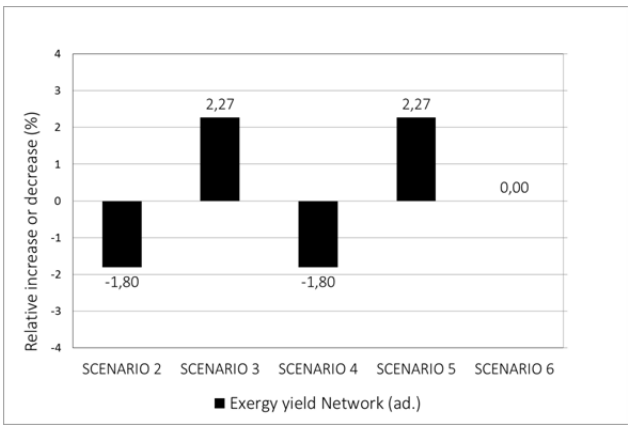
Analysing these balances allows the observation of several behaviours, some of them described below:

A decrease of network´s energy and exergy losses is observed for all those scenarios that establish a reduction of feed temperature, producing an increase of 1.33% in energy efficiency (Picture 1).

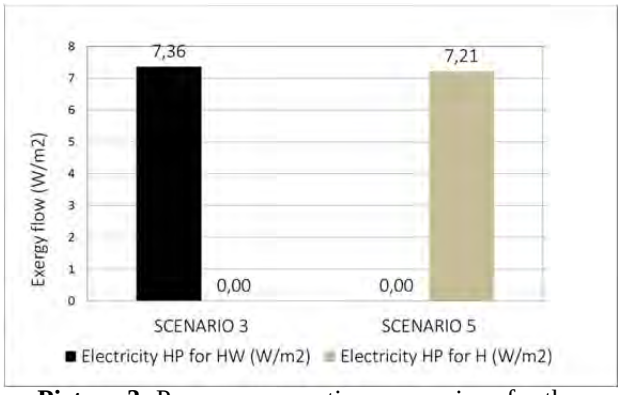
Furthermore, this situation leads to a 2.27% increase of the exergy yield (Picture 2).



Picture 1: Energy yield comparison respect to scenario 1



Picture 2: Exergy yield comparison respect to scenario



Picture 3: Power consumption comparison for the heat pumps

However, these improvements bring the introduction of heat pumps as a counterpart to support heating or hot water branches integrated within buildings' facilities. Picture 3 shows the high electrical power to be supplied to the heat pumps in order to heat domestic hot water (Scenario 3 = 7.36 W / m^2) or support the heating system (scenario 5 = 7.21 W / m^2), respectively.

CONCLUSIONS

The developed model worked correctly and without failures for the studied scenarios, being able to solve all equations systems accurately. Obtained results are realistic and coherent.

Both pros and cons for all scenarios were studied using exergy balances as a measurement of the system´s efficiency and power consumptions.

The present project analyses the real possibility of adapting the current Viennese thermal grid to a low temperature system, advancing towards the 4th generation of district heating networks [3].

An extension of this project is possible, in order to increase computation speed and improve the process of orchestration between the different softwares involved. In addition, there are other hypotheses that could be simulated, such as the introduction of renewable energies in combination with the district heating network

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CONSTRUCTION MATTERS: INCREASING THE EFFICIENY IN DESIGN AND CONSTRUCTION PROCESS

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INTRODUCTION

In a context where new concerns such as greenhouse effect, resource shortage and economical restoration are on the spot, the optimization of construction processes is a huge and required challenge, since the construction sector is the largest consumer of raw materials and energy in the EU (25-40 per cent) and its activities account for about one third of the whole waste generated and CO2 emissions annually [1]. Besides, it has evidenced a huge lack of productivity in the last decade compared to other industries. Therefore, new strategies are needed to redefine the whole sector towards a more industrialized resource-efficient design and construction process involving, among others, material performance, stakeholder participation and digitalization. Throughout it is estimated that 42% of the final energy consumption, 35% of the greenhouse gas emissions and more than 50% of all extracted materials could be reduced [2], being both environmentally and financially beneficial.

REFORMULATING CONTRUCTION THROUGH DIGITALIZATION

The path of actions are based on three main pillars: The use of timber as main material, in order to reduce the resource intensity of construction materials, and because of its high level of prefabrication performances; the development of multi-storey buildings optimizing within the resources used in a project; and the optimization of the whole design and construction process through digitalization and industrialization, focused on lean construction principles by eliminating waste, reducing costs, increasing team productivity and creating value [3].

Taking advantage of what has been seen in other industries such as the automotive or manufacturing, construction should aim to standardize and industrialize its processes through off-site construction, digitalization and a leaner process management [4]. A “digital twin” elaborated through a BIM model and a close cooperation between all the participants of a project on a very early stage, brings a consistent and structured data management what allows a reliable monitoring of all processes. An enormous productivity improvement is achievable in terms of material performance, but also in terms of time and costs. This productivity improvement is feasable not only on the design phase, but along the total life cycle following modifications of the real building and updating itself to predict performances and their impacts in order to totally succeed with the conception. However, this approach implies bigger efforts on the design phase and consequently higher initial

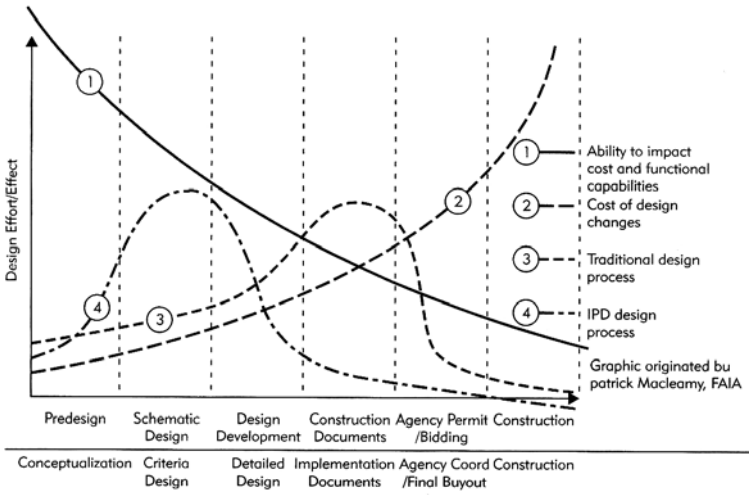

Figure 1: MacLeamy Curve. Abilities progression to control the costs and the costs of change in the traditional and IPD approaches

investment of time and costs, since every constructive element has to be firstly identified as sensitive to be part of a prefabricated system meeting all the required expectations (fire, acoustic, humidity, structural behaviour) and secondly accurately digitally modelled in a way it comes directly from design to production, avoiding the common fragmentation in traditional construction processes, where a number of different actors are participating at different stages of construction with poor levels of cooperation. This higher initial investment usually causes the rejection of the implementation of those approaches from side of many constructors, spite of the benefits they could bring later on by reducing up to 50% of the time spent on site. Nevertheless, its potential has been already proven in few pilot projects showing a large level of efficiency and productivity when combined with a leaner process management, as re-works and overlapping tasks are avoided, while quality, security and reliability are much higher.

DISCUSSION

One of these key projects, which unlock a new era of timber performance in multi-storey resource-efficient buildings, is the Life Cycle Tower One in Dornbrin, planed by the architect Hermann Kaufmann and built together with Cree by Rhomberg. All its construction elements were completely prefabricated in a factory, following the standards and modularisation defined through the system specifically developed for the project. This system was conceived in a way that its elements were prefabricated in local factories with the only need to be assembled on site like a Lego being able to raise two stores per day and with the possibility to replace them easily in the future if needed [5]. This approach brought lots of benefits in terms of CO2 emissions, costs, safety and quality, and since timber does not need the time to get dry as it is with concrete, beside its erection, works were developed parallel on site, saving up to 50 per cent of construction time. This shortness was translated to a significant reduction on the disturbances on traffic and neighbours caused throughout the construction phase. Additionally, this industrialised-based construction process allowed an quiet and clean on-site areal, where the space required for stock elements was minimal. These reasons above mentioned highlight the suitability of this kind of construction on urban areas.

CONCLUSION

Despite of these recent developments and the improvements achieved, design and construction processes on timber buildings still suffer a lack of efficiency in management. The aim of this work is to optimise these processes investigating the impact of different industrialised-based workflows and estimating improvements with the purpose to state a leaner value chain and stay competitive in the market of multi-store buildings, compared to concrete and steel, and to achieve a null-waste construction process in order to meet the expectation set by the EU, where all new buildings will be nearly zero-energy, highly material-efficient and zero construction waste sent to landfill by 2020 [2].

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ENGINEER'S PLAYGROUND: INTERFACING STUDENTS AND BIOREACTORS FOR TEACHING AND RESEARCH

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INTRODUCTION

Young graduates are an important driving force for the fourth industrial revolution. Therefore universities have to incorporate elements such as process simulation, automatization but also big data management in their study programs. Within the biochemical engineering work group E166-4 a web based system was established, which enables the direct accessibility of data from all bioreactors with a Python™and Matlab® programming interface. This eases data evaluation and enables the development and execution of real-time actions such as automatization and control without software limitations. Besides the successful use of the system in applied science, it was also used for lab courses in bioprocess engineering (e.g 166.164 LU Bioverfahrenstechnik) with positive feedback.

THE NEED OF A FLEXIBLE REAL-TIME LABORATORY ENVIRONMENT

Due to the high quality requirements of biopharmaceutical products, production processes are supervised by a growing diversity of sensors and analytical devices. To benefit from this increasing amount of information, data needs to be accessible in a manageable format. Whereas data scientists usually analyse historical datasets to extract knowledge, engineers mostly aim to maintain something under control. Therefore they need real-time access to the collected data and the possibility to act on them in time. Most commercially available devices (reactors, sensors, measurement devices) have a specific application and are limited in their extended use. Beside this, a significant amount of time is invested in data export, manual treatment and collection into data tables for later import into mathematical computing programs such as R, Python™, Matlab® and others, which enable to solve scientific exercises.

Figure 1: Real-time laboratory environment with easy accessible web interface

To overcome these barriers and to support students and researchers to realize their tasks and innovative ideas in a comfortable and efficient way,

a web based system was implemented in TU Wien's biochemical laboratories. The system is able to collect data from any physical device that supports any type of open platform communications (OPC). Through an intuitive web-interface (Django framework), which is shown in Figure 1, data can be visualized directly within the browser and compared to other running or historical processes. That way, running fermentation processes can easily be supervised from everyone, anytime and everywhere. Furthermore, selected data can be sent automatically to a running Matlab console or analysed directly in Jupyter notebooks (an interactive Python computing platform), where advanced algorithms can be implemented and executed. It was already successfully used for control of *Escherichia coli* and *Penicillium chrysogenum* processes and is the basis for further research in the fields of advanced monitoring and control.

INTERNET OF THINGS IN APPLIED TEACHING

Besides the quite obvious usefulness of the system for applied research, it could also be used successfully for teaching. To keep teaching up to date and to show and enable students to work in a digitalized industry, a practical laboratory course with a yeast fermentation process was extended by a modeling and data evaluation part. Now, in addition to learn how to conduct a real fermentation process, students are required to simulate a model [1] implemented in a Jupyter notebook. Furthermore, they have the possibility to simulate and parametrize the model using their recorded process data. Exemplary results can be seen in Figure 2. In this new course participants get first hands on, in working within a digitalized laboratory environment. Furthermore, the work with own data is motivating and helps the students to understand the interlink between modeling, simulations and real process data. Finally the course extension has broaden the view of participants and increased the acceptance to work intensively with data.

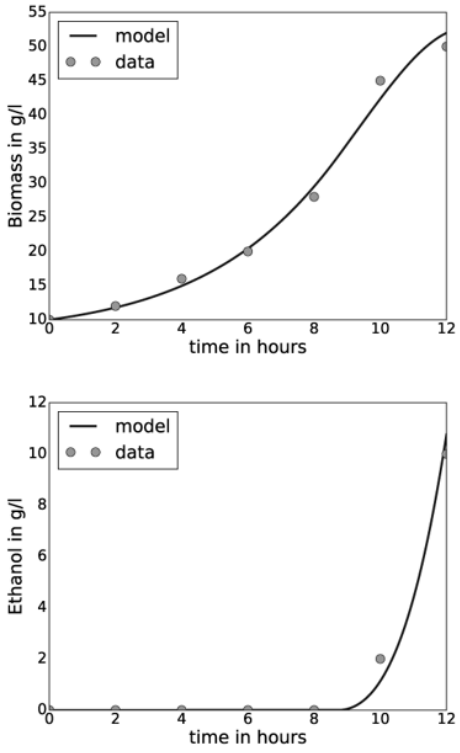

Figure 2: Application example: Model parametrization

CONCLUSION & OUTLOOK

A flexible real-time laboratory environment is an important basis for fruitful research in the field of bioprocess engineering as it enables the realization of innovative ideas. Furthermore, it opens up new perspectives in interactive teaching enabling to bridge offline simulations of models with real data and to bring young graduates closer to the vision of industry 4.0.

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IN-FIELD SIMULATION FOR PROCESS TUNING IN INDUSTRY 4.0 APPLICATIONS

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INTRODUCTION

Modeling and simulation approaches are well embedded into today's development flows for industry 4.0 applications. Model-based design, virtual prototypes, and virtual commissioning enable cost-efficient verification and optimization during the design phase. Unfortunately, in many cases, the use of simulation processes ends as soon as a design is deployed to production. The approach of the presented work is to migrate simulations to the operation phase of a production process. Therefore, so-called in-field simulation methods, monitor the current process state and simulate its behavior for a limited future time period. The simulation results are then used for analysis and subsequent tuning of parameters with the goal to optimize the production process under a specific objective (e.g., efficiency, throughput). This described in-field simulation procedure has even more impact if besides classical functional simulation potentially occurring uncertainties are considered. For example, in industry 4.0 applications such uncertainties can be unpredictable changes in environmental conditions (temperature, humidity, etc.), reduced availability of controllers caused by variations of QoS parameters in communication channels, variations in the performance of electronic components, etc.

CHALLENGES OF THE APPROACH FOR INDUSTRY 4.0 APPLICATIONS

In this section, we identify and discuss some challenges and of course advantages of the introduced in-filed simulation approach for industry 4.0 smart factory applications.

Models and simulation software: Models used for the design process has to be migrated to in-field simulation. A critical part is the abstraction level of the models which directly reflects the complexity, finally affecting the performance of the in-field simulation. For this work, we use C/C++ based models derived from high level behavioral SystemC [3] descriptions of the application. Also, a model of the process environment has to be integrated into the simulation. Uncertainties are represented as parameter deviations in models which consequences that values in the system no longer are represented numerically but as ranges. However, modeling uncertain parameters is getting increasingly challenging due to the rising number of variabilities and complex uncertainty effects (e.g., dependencies). Thus, classical onte-Carlo based methods will be no longer sufficient, and new semi-symbolic and formal approaches may come into play [1].

Computation resources: As illustrated in Figure 1 in a smart factory application there are numerous computation cores integrated in the included automation components such as robots, PCs, Panels, etc. Some of the processing resources may be permanently or partially unused (indicated in red in the figure). These resources may be loaded with the proposed in-field simulation software. However, these resources may be very diverse and distributed.

Process optimization and decision-making: Optimization and decision-making algorithms are primarily essential for the performance of the full production process. Thus, optimization procedures based on the results obtained form in-filed simulation runs, have to be explicitly defined for a given application including a behavioral model of the system's environment [2]. However, innovative en-

hanced technologies such as machine learning, collaborative decision-making algorithms and blockchain techniques are potentially applicable.

Observability, controllability: A requirement for the smart factory process itself is that there is adequate sensor equipment installed. The current state of the production process has to be observed continuously. This data is a basis for the execution of simulation runs. Further, the process parameters have to be tunable in a way to maximize the performance even under the presence of uncertainty.

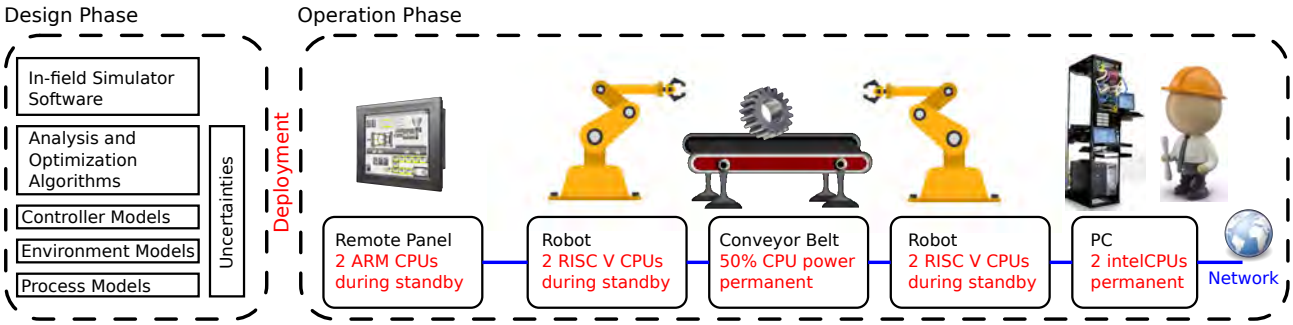

Figure 1: An industry 4.0 smart factory application including unused computation resources executing in-field simulation software

FIRST RESULTS AND DISCUSSION

For a first prototype implementation, we used the system simulator SystemC [3] in combination with a C++ library for semi-symbolic uncertainty modeling. Both is compiled for the ARM processor architecture. The simulation is then deployed on a Raspberry Pi platform. Until now our research focus is more on the management and distribution of the simulation software modules in available processing cores in the field. However, there is an ongoing experiment using the proposed in-field simulation concept for a smart lighting application.

CONCLUSION AND VISION FOR SMART CITIES

As described in the second section we highlight our operation-phase simulation for an industry 4.0 smart factory applications. However, our approach is extendable for smart cities. In such an architecture partially free computation resources are available nearly everywhere. All of them are in principle somehow connected to the internet. Our vision is to realize a collaborative simulation application for optimizing processes in the smart city. Such processes are for example smart power grid applications where the generation of energy has to be planned under the presence of uncertainties in the grid load. Besides the technical implementation, in smart cities also new business model for providing, managing and utilizing in-field simulation resources are possible, which potentially makes the approach very attractive for customers.

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COMPUTATIONAL PREDICTION OF SOUND PROPAGATION IN URBAN CANYONS

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INTRODUCTION

Problems associated with increased noise exposure – especially due to road traffic in the urban context – are well known[1]. However, the acoustic planning of outdoor urban areas and the potential of simulation still does not receive sufficient attention. The present contribution focuses on urban canyons via comparison of measured and simulated sound levels of two inner-city areas in the city of Vienna, Austria. The research includes also a sensitivity analysis that takes into account variations in model assumptions. This makes it possible to explore the calibration potential of acoustical simulation tools in urban planning applications.

INPUT DATA DERIVATION

The workflow included the implementation of the real locations with carefully chosen first approximations with regard to input data. Towards this end, geometry data was obtained from an existing repository and subsequently adjusted to fit the input requirements of the selected application. Furthermore, multiple sources of information were used to specify material properties such as the absorption coefficients of the relevant surfaces. Similarly, assumptions pertaining to the sound power of pertinent sources were made based on applicable standards[2] and in-situ observations. Similarities and differences between the two locations could be thus established. Moreover, modelling considerations with regard to the level of details and the sky representation were investigated.

IMPACT ANALYIS

The first simulation results were contrasted to in-situ measured datasets obtained at different heights above the ground in front of the facades. Furthermore, scenarios with different surface characteristics, traffic flow, receiver positions, weather conditions, and simulation tool's settings were generated from the baseline model and their level of impact on sound pressure levels (SPL) was studied. The datasets were analysed and compared considering the linear SPLs and their root mean square deviation (RMSD) over the octave bands from 63 Hz to 8000 Hz. Thus, the level of impact, the direction of the change, and the degree of frequency dependency of the results by the alteration of input parameters were captured.

RESULTS AND DISCUSSION

The results of the contribution are twofold. On the one hand it provides a methodology and a systematic overview on input data that is needed for using room acoustic simulation tools for urban sound propagation applications. On the other hand, it uncovers the potential of such simulations through a comparison with measured data and a sensitivity analysis. The agreement between simulations and measurements were found to be satisfactory. However, the level of congruence is a function of frequency. Thereby, lower bands usually display higher deviations. The impact of input parameters was characterized both by the SPLs and RMSD. Additionally, a classification of scenarios into high, moderate and low impact categories was considered. Furthermore, the impact of

frequency band and receiver position was explored. The results show that modelling considerations such as the sky representation and the vertical closing surfaces of streets have low impact on the results. Likewise, room setup settings such as number of late rays and impulse response length does not affect SPLs unless they are set to an insufficiently low level. Hence, reliable results are obtainable already at a rather low computational cost. Also, it was found that small alterations in the absolute values of absorption and scattering coefficients did not influence SPLs to a great extent. Similarly, weather conditions are of interest only in case of high uncertainties regarding temperature or relative humidity, and even then, only high frequencies are affected to a noticeable degree. On the other hand, the scenario with fully scattering surface properties resulted in a significant rise of the SPLs, while a significant increase of the facades' absorption caused a remarkable fall of the same metric. Moreover, even moderate and realistic variations in the traffic flow characteristics such as vehicle speed and traffic density caused a notable deviation of the results. Larger differences between measured and simulated datasets can occur, especially at low frequencies. These may be attributed to the insufficiently accurate representation of the time varying traffic flow and sound propagation at low frequencies.

CONCLUSION

Overall, it was found that sound propagation in urban canyons can be modelled by a room acoustic software with good precision and at a low computational cost. In general, the findings suggest that little changes have small impact and even a high degree of simplification of the geometry is permissible. Therefore, if the order of magnitude of the input data is appropriate, then the simulation yields reliable results, in agreement with the in-situ measured SPLs. On the other hand, the results suggest that a more sophisticated urban situation, which includes miscellaneous objects such as trees and parking cars or an urban canyon, which has a lower height to width ratio can introduce additional uncertainty in input parameters. Consequently, a higher degree of deviation of the results from the reference can be expected. Moreover, the impact analysis uncovered the most influential input parameters, namely characteristics of the road traffic and surface quality of the materials, which could be of interest of urban planners in future. Accordingly, further research should concentrate on the impact of traffic composition on one hand, and additionally, explore the potential of implementing acoustically effective external finishing for building surfaces. Furthermore, simulation results gained at different weather conditions could be analysed in the context of in-situ measurements. Additional analysis of the geometric attributes of the input model could also be useful. Finally, different national standards with regard to the sound power attributable to road traffic could be compared in view of their impact on the SPLs.

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Research Field *Novel and Smart Materials*

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Introduction

Recent global challenges in the fields of environment, energy, and natural resources require new approaches to technological and industrial processes in order to improve efficiency and to reduce the ecological footprint. Furthermore, new technologies can trigger paradigm shifts in our daily lives, by improving safety, comfort, or health.

The development of Novel Materials plays a major role in this area. In many cases, conventional materials are already used at their intrinsic limits, with respective limitations in mechanical or thermal stability. In other cases, the scarceness of resources or political turmoil require the search for alternative compounds.

As such, Novel Materials are needed to further enhance the application range of existing processes or to facilitate completely new technological approaches. The need for the development of new materials can be found in all material classes, including polymers, metals, ceramics, glasses, and composites, as well as so-called biomaterials; and further includes the provision of specific structures in many shapes and forms, ranging from thin films and fibers to micro- and nanostructured surfaces and bulk materials, depending on the prospective application.

In addition to the development of new materials, a special focus of this symposium topic is set on Smart Materials – solid, liquid, or gaseous compounds which react to an external stimulus by changing one or more of their properties, without further external action. Examples for external stimuli can range from temperature, mechanical stress, to electric and magnetic fields. Smart Materials can be used in a wide range of applications. Examples include piezoelectrics, pH-sensitive polymers, OLEDs, shape memory alloys and polymers, self-healing materials, or materials suitable for energy conversion, including thermoelectrics.

This symposium topic is primarily represented by the Materials and Matter research focus of TU Wien, but the interdisciplinary nature of this topic implicates the crossover to the other focal areas. As such, we welcome and invite contributions from diverse research fields and the respective Faculties at TU Wien involved in the development and application of Novel and Smart Materials, including Physics, Civil Engineering, Mechanical and Industrial Engineering, Electrical Engineering, or Technical Chemistry.

HETEROSTRUCTURE FORMATION IN III-V NANOWIRES GROWN ON SILICON

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INTRODUCTION

III-V nanowires (NWs) have potential applications in many fields, from optics and electronics [1], to solar cells [2] and beyond. While many of the predicted 1D effects in NWs are proving hard to confirm experimentally, currently much promise in the field comes from the growth of heterostructures. This is achieved through growth of lattice mismatched materials, which is facilitated in NWs due to their relaxed strain conditions [3], or crystal-phase engineering [4], both of which present exciting opportunities for band engineering in nanostructures.

The research reported here is concerned with the growth of lattice-mismatched III-V materials in various NW geometries. An overview of electrical and optical properties of these heterostructures will be given, along with the discussion of their growth and potential device applications.

MATERIALS AND METHODS

In this study, NWs were grown via self-catalyzed molecular beam epitaxy (MBE) on Si(111) substrates. Optically we have studied $In_{0.16}Ga_{0.84}As$/GaAs, where $In_{0.16}Ga_{0.84}As$ (band gap at room temperature: 1.196eV) forms quantum wells in GaAs (band gap at room temperature: 1.42eV). The NWs incorporate multiple InGaAs quantum wells formed radially by core-shell growth. Electrically we have studied GaAs/BGaAs, where the bandgap of BGaAs is hypothesised not to deviate greatly from that of GaAs, but due tothe small lattice constant of BAs and other anomalous properties, growth in planar geometry has proven difficult.

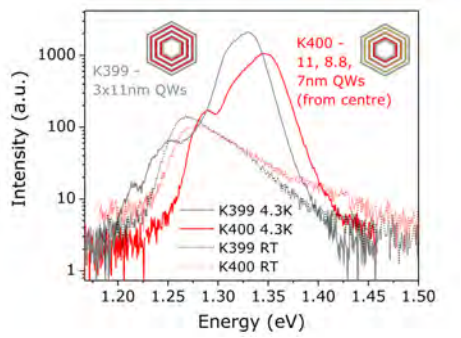

Figure 1: Photoluminescence measurements taken on multi-quantum well GaAs/InGaAs nanowires at room temperature and 4.3K. Inset are the schematics of the radial NW quantum wells.

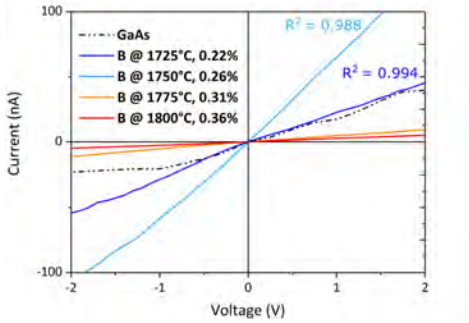

Figure 2: Two-point IV measurements taken on GaAs/(B)GaAs nanowires, with an undoped GaAs reference

Optical measurements were performed with a commerical confocal photoluminescence (PL) setup (Witec Alpha 300). NWs were excited in continuous wave mode via a fiber-coupled 532nm sapphire laser, and the PL spectrum was coupled through a blazed grating spectrometer (BLZ 760nm) enhanced for visible/near-infrared emission. Spectra were recorded on an Andor iDUS CCD cooled to -60C. Measurements were taken

at room temperature, or mounted to copper plates and measured at 4.3K in a He closed-cycle cryostat.

Electrical measurements were taken on NWs dispersed on 50nm thermal SiO_2 on Si substrates contacted in 2- and 4pt geometries. Contacts were defined via e-beam lithography and p-type contacts (Au/Zn/Au, 5/10/100nm) were deposited in a Balzers thermal evaporator. This contact metallization was chosen in anticipation of the fact that boron in GaAs acts as a doubly-charged acceptor when incorporated on As sites [5].

RESULTS AND DISCUSSION

Photoluminescence measurements on $In_{0.16}Ga_{0.84}As$/GaAs multi-quantum wells (figure 1) is blue-shifted when the outer quantum well is thinner, regardless of the inner quantum well thickness. This means that recombination of carriers occurs preferentially in outer quantum wells, which suggests that there is downwards band-bending in the NW heterostructure, thus carriers diffuse preferentially to the nanowire edge, regardless of where in the NW they are excited. This is an effect that we would like to further investigate by looking at the surface states and band alignments of our structures, as well as through measurements exploring the carrier dynamics in the NWs.

Electrical measurements on GaAs/(B)GaAs nanowires are shown in figure 2. Adding a small amount of boron during growth disrupts the normal growth process, leading to boron atoms incorporating on antisite defects, where they act as doubly-charged acceptors. This leads to p-type doping of the NWs, which is evident in the fact that Ohmic contacts are formed to NWs at all boron concentrations.

CONCLUSION

The results presented here have an interesting impact on the growth of radial NW heterostructures containing lattice-mismatched III-V materials. BGaAs has never been grown in nanowires, and we have shown for the first time its potential for use in such structures, while highlighting some of the difficulties in its incorporation during growth. At the same time, the fact that recombination preferentially occurs in the outer NW shells must be taken into account when designing band-engineered structures in NWs. The eventual aim of this research is to design such band-engineered structures exploiting the optical and electrical properties of the constituent materials.

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PERFORMANCE EVALUATION OF VARIOUS FINISHING LAYERS FOR AEROGEL PLASTER

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INTRODUCTION

In recent years, many efforts have been undertaken to investigate potential energy-efficient renovation solutions for existing buildings, especially in case of historical buildings. Applying thermal insulation systems to exterior building envelope is one of the most common strategies to reduce building energy use. In this regard, using new insulating nano-material with special hygro-thermal properties, such as Aerogel, has become increasingly common worldwide. This paper describes the result of a case study on application of various finishing layers on Aerogel plaster, which were applied on the external layer of a retrofitted construction.

Silica Aerogel is an open-cell nano-material that is suitable for applications where particularly high thermal insulation properties are desired[1]. An insulation coating based on silica Aerogel has a minimal impact on the thickness of the walls, and is a lightweight refurbishment system with high thermal performance (low thermal conductivity, i.e. 0.014 W.m-1K-1, and low density, about 3 kg.m-3)[2]. In addition to the thermal performance, the hydrophobic behavior of an Aerogel based material is useful in building renovation. Applying the rendering on the external surfaces reduces or eliminates the undesirable consequences of condensation and moisture problems within the wall structure[3].

METHODOLOGY

The case study in this paper is an office area in the historical building of TU Wien, Vienna, Austria. The old wall construction of the case study (with three layers, including gypsum plaster, hollow brick masonry, and lime cement plaster) was retrofitted by applying a plaster system encompassing a highly-insulated Aerogel layer (Fixit 222)[4] on the existing construction (Figure1). Four different combinations of exterior plaster Röfix together with Röfix PE [4] colour coating were applied on the aerogel layer, to harden the surface and give it a better grip (Table 1, field S1 to S4).

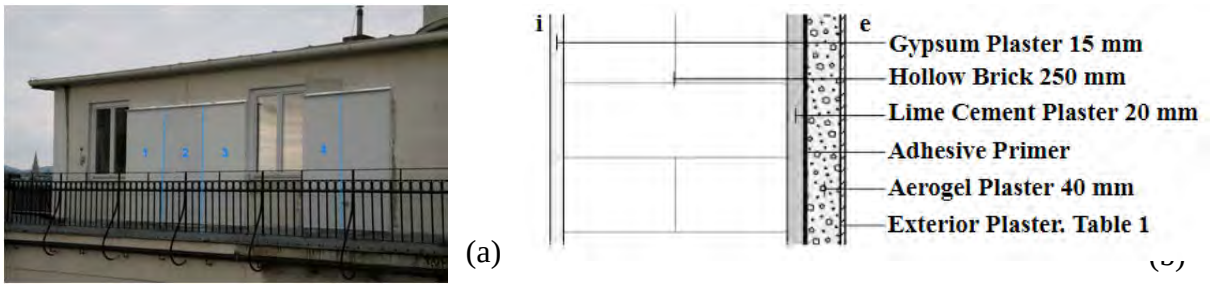

Figure1: Tested Façade with the marked locations of fields 1 to 4 (a), and a section of the layers (b)

To study the hygro-thermal performance of the wall, as influenced by different choices of the abovementioned fields, a set of sensors were installed within different layers of the construction. This enabled the in-situ measurement of temperature and relative humidity within the layers. This study utilizes the monitored data from the winter period 2013/2014.

Table 1: Combinations of exterior plaster of fields S1 to S4

Field	Plaster	Silicate paint	Sd-Value (m)	μ - Value	Remarks
S1	Röfix 380 fine grained	Röfix PE 819 Sesco, lime wash	0.0002	12-15	Diffusion open, stores moisture
S2	Röfix 750 coarse grained	Röfix PE 225 Reno, silicate paint	0.01	20	Diffusion open
S3	Röfix 380 fine grained	Röfix PE 819 Sesco, lime wash	0.0002	12-15	Diffusion open, stores moisture
S4	Röfix 380 fine grained	Röfix PE 419 Etics, silicon resin paint	0.1	12-15	Diffusion open, water repellent

RESULTS AND CONCLUSION

In order to investigate the humidity level and condensation risk, specific humidity values were studied. The boxplot in Figure 2 illustrates the specific humidity distributions in different layers, showing the minimum, maximum, mean and range of the data in different fields. The results presented here illustrate that the specific humidity values in different layers are not significantly affected by the choice of different exterior plasters. In fact, other features of this layer, such as the appearance (i.e. fine versus coarse grains), are more relevant for the selection of one field over the other options.

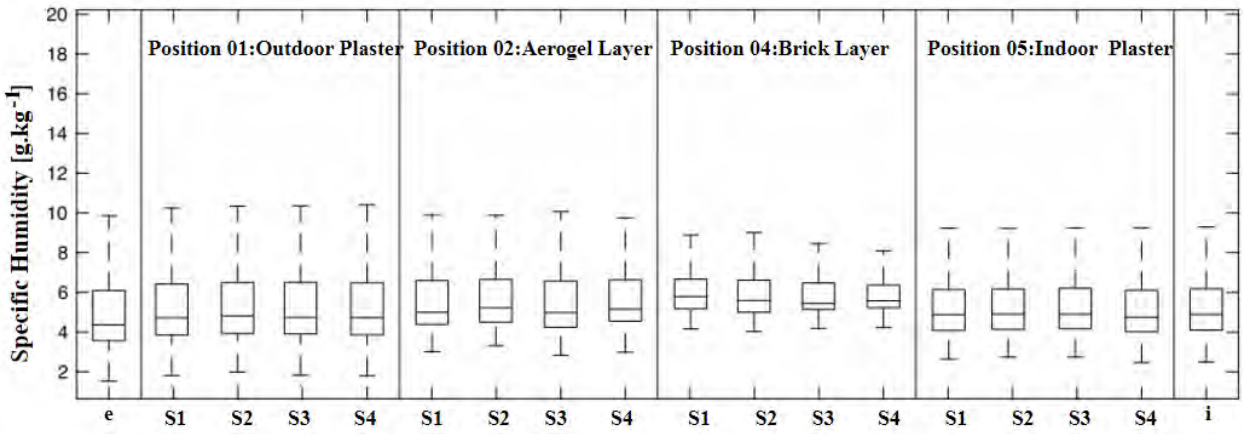

Figure 2: Specific humidity of fields S1 to S4 in different position of the construction in winter 2013-2014

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POROUS POLYMER DERIVED SiCN-CERAMIC WITH DIRECTIONAL PORE STRUCTURE OBTAINED BY FREEZE CASTING

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INTRODUCTION

Porous ceramics are interesting materials as substrate of membranes or catalysts because of their high inner surface area, their excellent mechanical as well as thermal properties, and their chemical stability. Polymer derived ceramics (PDC) offer wide possibilities in new processing methods, easy shaping and are especially interesting for new pore templating approaches[1].

Freeze casting is a technique to obtain aligned pores in ceramic materials in general and in PDCs in particular. So far, only SiOC and SiC ceramics have been processed in this manner, using solid preceramic precursors such as polysiloxane or polycarbosilane[2]. To obtain SiCN, poly(vinyl)silazane (PSZ) is generally used, which is a liquid precursor. The aim of this work is to develop a processing routine for freeze casting PSZ with a focus on crosslinking the precursor at low temperatures.

MOTIVATION AND EXPERIMENTAL

Liquid poly(vinyl)silzane is generally crosslinked at elevated temperature to obtain a solid green body. As freeze casting is performed at temperatures below the freezing point of the solvent, thermal crosslinking of the precursor is not possible without destroying the structure of the solidified solvent, which acts as pore directing agent.

By employing a photopolymerization technique,[3] it was possible to crosslink PSZ at low temperatures. The pore structure directed by the dendritically grown solvent was not affected or destroyed. Subsequently, the solvent was removed via sublimation, leaving crosslinked PSZ as the negative image of the crystallized solvent. To enhance green body strength, the prepared samples were thermally crosslinked before they were converted into ceramic materials at 1000 °C in nitrogen atmosphere.

The amount of precursor in the mixture precursor/solvent and the cooling rate while freeze casting were varied to evaluate the respective influence of these parameters on the resulting pore structure as well as porosity.

RESULTS AND DISCUSSION

PSZ was successfully crosslinked at low temperatures using a photopolymerization technique, conserving the structure of the solvent acting as pore template. An increase in PSZ content in the starting mixture leads to narrower pores and higher number of pores, shown in figure 1. Furthermore, it was shown that the total porosity follows a linear trend in dependence of initial PSZ content. The effect of the cooling rate is shown in figure 2. Cooling at high rates results in more ordered pore structures than cooling at low rates.

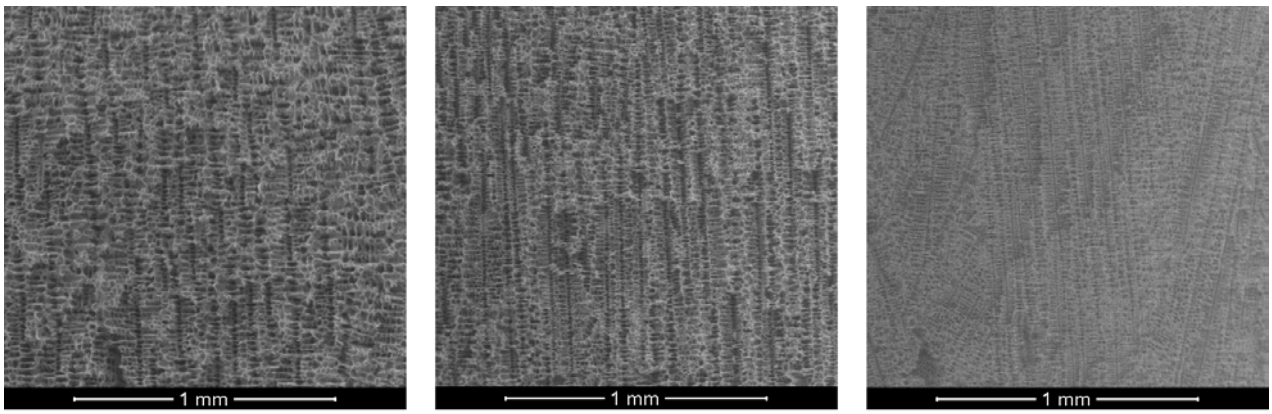

Figure 1: Pore structure of pyrolyzed specimens as a function of initial PSZ content (SEM micrographs of sections parallel to freezing direction).

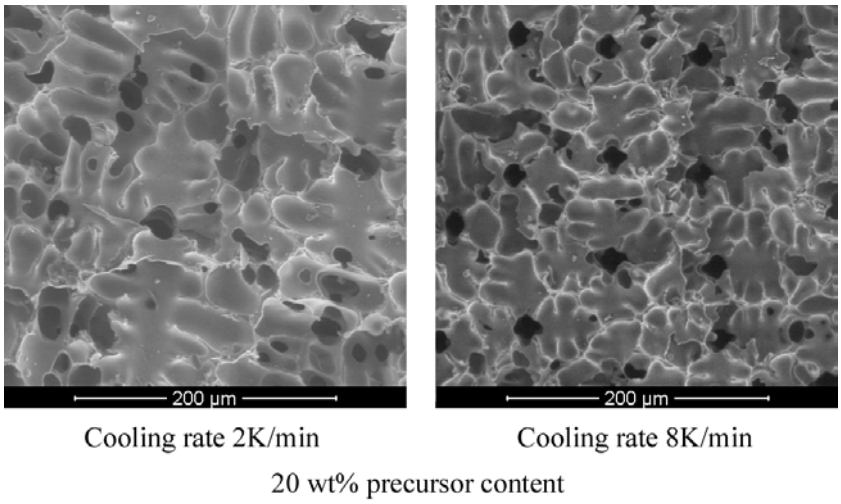

Figure 2: Pore alignment depending on cooling rate during freezing (SEM micrographs of sections perpendicular to freezing direction.

CONCLUSIONS

Using a photopolymerization technique, it was possible to generate porous SiCN ceramic with directional pore structure derived from a liquid poly(vinyl)silazane precursor by shaping via freeze casting. The initial polymer content in the solution as well as the cooling rate during freezing significantly influence both pore structure and total porosity. Even though a practicable routine for producing samples has been developed, further development involving the polymerization step is required in order to minimize crack formation. Furthermore, samples will be further characterized using Hg-porosimetry, testing of mechanical properties, and testing of gas permeability.

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DIGITAL MATERIALS: A HYBRID 3D-PRINTING SYSTEM

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'Photopolymers in Digital and Restorative Dentistry'

INTRODUCTION

Additive manufacturing (AM) has developed into a promising technology for various applications and provides advantages over conventional manufacturing methods like casting or milling. Drawback of most commercially available systems, however, are the insufficient mechanical properties and the limited resolution of the printed parts. With industry calling for tougher and stronger materials, especially for engineering applications, we developed a stereolithography (SL) process based on the principal of digital light processing (DLP), combined with direct inkjet printing. With this, we are able to print highly viscous photocureable resins with high resolution and excellent surface quality and mimic the thermo-mechanical properties of natural structures like nacre by jetting thin layers of soft material into a hard matrix. Those so-formed "digital materials" show promising results regarding enhancement of the thermo-mechanical properties, as first experiments indicate an increase of the strain at break and impact strength by over 50% and 40%, respectively – compared to the plain matrix material.

FUNDAMENTALS OF THE PROBLEM AND EXPERIMENTS

In nature, many biological materials are known to be both stiff and tough, such as biosilica or nacre[1]. The combination of tough protein and stiff mineral results in extraordinary mechanical properties exceeding those of the single components by far. The structure of those materials has a determining influence on the toughening of the materials, possibly resulting from crack deflection at weak interfaces in layered structures[2] or shielding effects by local variation of material properties[3]. Replication of such materials is difficult and is best done by manufacturing delicate laminates. Therefore, the layerwise buildup of 3D-printed structures has potential to reconstruct nacre-like materials, even exceeding lab scale. Advantages of stereolithography as AM technology are the high resolution and surface quality of the printed parts as well as the possibility to process high viscous materials. However, conventional SL machines allow the processing of only one material at once. We therefore developed a DLP-based SL process and combined it with a direct inkjet system. In the first step of the process, a material vat is coated with an acrylate-based resin. A digital micromirror device (DMD) projects blue light (light emitting diodes with a wavelength of 460 nm) onto the resin and cures it layer by layer, forming the matrix of the printed part. In a second step, the building platform rotates and a high-resolution print head selectively places elastomer droplets onto this previous layer, which then are cured during the next stereolithographic step. In order to evaluate the influence of the inkjet-layers, specimens with different elastomer content – without ink ('Reference'), every 2nd layer ('50%'), and each layer ('100%') – were printed. DMA measurements, tensile and impact tests were performed to measure the thermo-mechanical properties and their modification.

RESULTS AND DISCUSSION

DMA measurements showed a slight decrease of the storage modulus at room temperature, resulting from an overall softening of the material by adding elastomers. However, the glas

transition temperature T_g was constant for all specimens. Decreasing tensile strength of 15% ('100%' compared to 'Reference') could be observed during tensile test, but a significantly higher elongation at break (+55%) is a promising result (see Chart 1).

(a) (b)

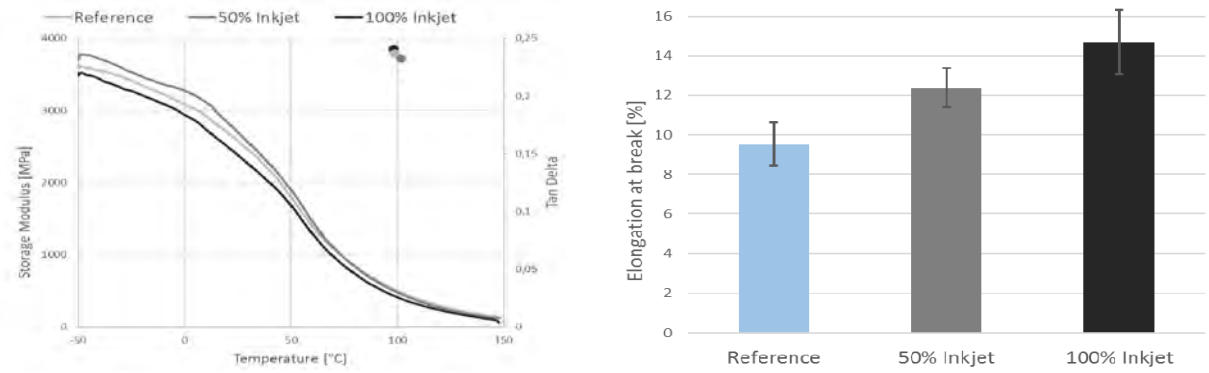

Chart 1 DMA measurements (a), but results in significantly higher elongation at break (b)

Dynstat impact tests of samples with three different ink-layer orientations showed an increasing toughness for all building directions by 25 – 45% (see Chart 2). In addition, creep behaviour was not influenced by jetting ink-layers into the part.

(a) (b)

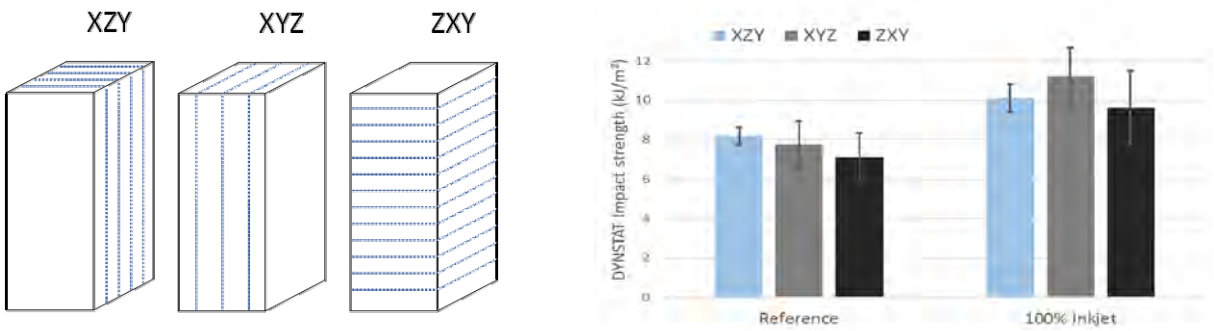

Chart 2 Different jetting directions, correlating the building direction of the printed part (a). In each direction, a significant increase of the impact strength was observed (b)

CONCLUSION

The first feasibility analysis shows promising results, as elongation at break and impact strength could be increased without significantly weaken the material. Apart from toughness modification, this novel technology allows further modifications of the printed parts in a way, which has not been feasible up to now: conducting tracks inside complex shaped parts, surface modification with inorganic materials, customized coloring and other multimaterial approaches can be established.

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EXPLORING THE TECHNICAL REQUIREMENTS OF VACUUM GLAZING FOR CONTEMPORARY WINDOW CONSTURUCTIONS

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INTRODUCTION

Vacuum glass has been considered as a potential solution for energy-efficient transparent building assemblies. In recent years, the industrialized production of vacuum glazing has become more common. It can be expected that such products will be more frequently deployed in the building sector. Previous efforts in research and development mainly focused on the development of the vacuum glass itself, due to the challenges regarding durability of the glass (specifically, long-term preservation of vacuum in the interstitial space). Less attention has been paid to the construction detailing of windows equipped with vacuum glass. The properties of vacuum glazing are different from those of regular insulation glass. Thus different approaches to window construction are required. This contribution presents the structure and findings of a recent research project, focusing on design and construction of windows with vacuum glazing. Thereby, various performance aspects of different frame/glass constructions were examined. The thermal performance, one of the research foci within this project, was assessed in a two-fold manner: On the one hand, knowledge of previous studies pertaining to vacuum-glass application in historic window constructions was obtained and processed. On the other hand, numeric thermal bridge simulation was applied to evaluate different frame designs and to derive their performance indicators. Moreover, in the framework of the project, different innovative window detailing approaches were explored using simulation and functional prototypes. This contribution provides an overview of the research project, developed window construction designs, and their performance.

VACUUM GLASS

The term vacuum glass denotes here two glass panes with an interstitial distance of 0.15 to 0.5 mm and a tight edge seal around the component. Additionally, the interstitial space has a grid of distance holders (so called pillars) that keep the distance between the two glass panes. This is important, as the interstitial space is evacuated via an opening that is later sealed. Without the pillars the two glass shells would bend against each due to the surrounding atmospheric pressure. As this solution radically reduces conductive and convective heat transfer, the glass is highly insulating. Conduction occurs in the edge seal and through the distance pillars. Convection is practically eliminated, as long as the vacuum layer persists. The third heat transfer mechanism – radiation – is not affected by the evacuation. However, via application of low-emissivity foils, radiative processes could be influenced as well. Given the described setup, it seems clear that the edge seal and the pillars would represent potentially weak spots in the construction. In a previous study [1], the effect of the pillars regarding heat conduction was found to be very small, due to their very small dimension. Thus, the appropriate consideration of the edge seal in window construction forms the most important thermally relevant requirement for windows employing vacuum glazing pertaining to thermal performance.

WINDOW CONSTRUCTION WITH VACUUM GLAZING

During the past decades, the window industry in central Europe has contributed to a number of innovations in window construction. These include the introduction of double and triple glazing, the application of low-emissivity layers, the introduction of rubber seals, and the utilization of different construction materials, such as aluminium (as weatherproofing for timber frames). However, the fundamental construction principles regarding frame construction and operation possibilities (usually turn-and-tilt windows that open inwards) have not fundamentally changed. The introduction of vacuum glazing can be considered as an opportunity to new and innovative solutions. In the research project MOTIVE, different new window construction options with vacuum glazing were designed and extensively studied. Thereby, multiple issues were addressed, including construction possibilities, thermal and acoustical performance, usability, operability, and aesthetics. Specifically, seven design concepts were examined at different levels, ranging from conceptual sketches to full-fledge window mock-ups. Figure 1 illustrates a number of such concepts and associated level of investigation.

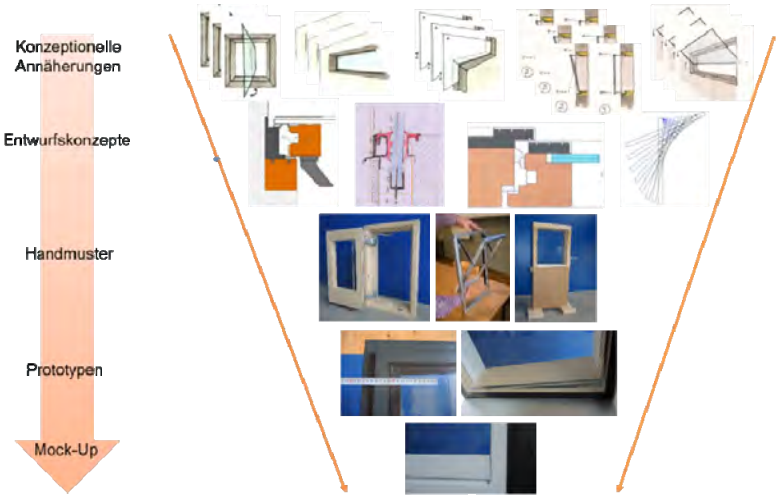

Figure 1: Examined window design ideas (and investigation depth).

RESULTS & CONCLUSION

The main results of the project suggest that, given the availability of construction fittings and seals, the proposed designs could be developed into windows with a performance matching those of common triple glazing windows, but superior in view of assembly thickness and weight. Some of the designs showed advantages in handling and maintenance (cleaning), while for other design ideas these aspects are not fully resolved. The resulting vacuum glazing prototypes encouraged the authors to initiate a research and development effort initiative together with key partners from window industry toward high-performance market-ready window products incorporating vacuum glass.

ACKNOWLEDGEMENT

The presented research efforts were in part funded by the Austrian Research Promotion Agency (FFG, project MOTIVE, project number: 854690).

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LOW ENERGY ION SCATTERING (LEIS) – INTRODUCTION TO THEORY AND PRACTICAL APPLICATION

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E165 Institute of Materials Chemistry

INTRODUCTION

In heterogeneous model catalysis, electronic, geometric and chemical properties of metallic surfaces decide whether certain chemical reactions take place or not. Over decades, many different characterisation methods were developed which are based on the interaction of sample surfaces with either probe particles (photons, electrons, ions, atoms) or applied fields under ultrahigh vacuum (UHV). Though, the most significant obstacle is the surface sensitivity and only very few techniques describe the topmost atomic layers exclusively. One of these techniques is LEIS and it features a series of advantages over other eligible methods.

THEORY AND EXPERIMENTAL

Theoretical aspects of LEIS are presented in analogy to a game of billiard. In doing so, fundamentals that should facilitate interpretation of spectra for users are discussed, as well as the origin of the method's ultimate surface sensitivity. The focus is on determining the chemical composition of the utmost atomic layer of solid surfaces, in particular that of metallic alloys or intermetallic compounds, which are important substrates for growing model catalysts. Preserving the chemical and structural integrity of the topmost atomic layer during analysis poses a great challenge. However, scattering of low-energetic He^+-ions keeps the investigated surface intact and also offers utmost surface sensitivity, which is a unique combination in surface analytics.

As an example for the practical application of LEIS, a new $Pt_3Zr(0001)$ single crystal was used, which provides the opportunity to grow an ultrathin ZrO_2 film. ZrO_2 is a material of highest interest, especially concerning current research on solid oxide fuel cells (SOFC) and related catalytic properties. The synthesis of a ZrO_2 film through deposition of Zr under UHV by common techniques (e.g. electron beam evaporation) is difficult because Zr has a high melting point and a low vapour pressure at the melting point.[1]

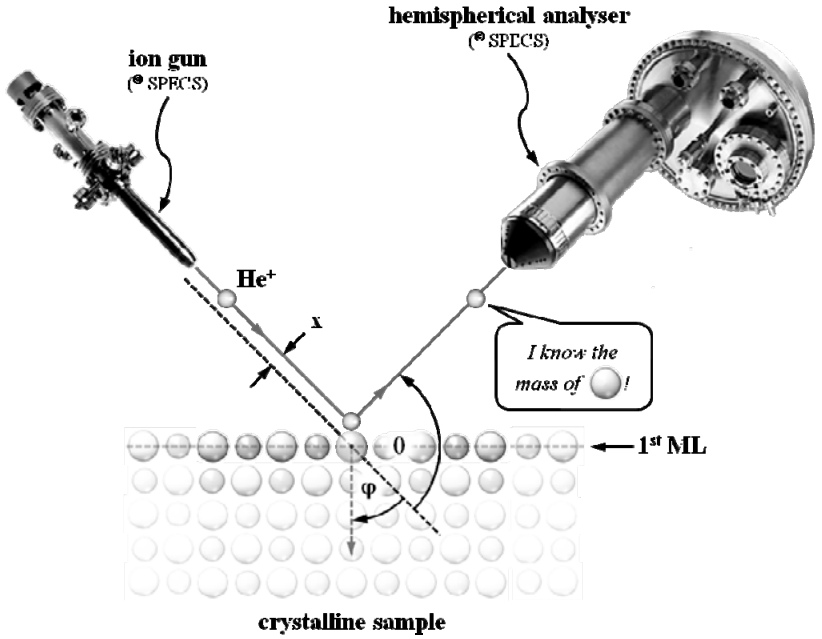

Figure 1: Sketch of the experimental setup

Nevertheless, it has been reported in literature, that oxidation at elevated temperatures liberates the Zr from the top atomic layers and a thin ZrO_2 film is formed.[2] In this way, continuous ZrO_2 thin films are accessible with uniform surface structure, and with a high reproducibility. However, this only works if the surface of the single crystal is clean and has the correct stoichiometry. Up to now,

scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) have been applied to study the surface structure of alloy and oxide film.[3] LEIS experiments complement chemical information on the surface of this model system. In addition, LEIS may also shed light on the thermal stability of metal nanoparticles (e.g. Ni), deposited onto the ZrO_2 film. These represent catalytically active centres of SOFC anodes.

The implementation of LEIS requires an accurate geometric arrangement of the ion source, the sample and ion detector inside the respective UHV setup. This means that the ion beam, being invisible to the human eye, must be focussed onto the sample. Therefore, a Au/Cu-target was designed to adjust the sample position and spot size of the ion beam, aiming for the strongest possible Au-response. Optimum settings of the manipulator and ion gun yielded an accuracy of roughly 83.3 at-% of Au.

RESULTS AND DISCUSSION

In order to determine the chemical composition of the topmost atomic layer of $Pt_3Zr(0001)$, quantification was carried out by employing polycrystalline metal foils (Pt, Zr) as elemental standards. Also, a polycrystalline Ni foil was measured, enabling the quantification of Ni nanoparticles on $ZrO_2/Pt_3Zr(0001)$. After performing extensive cleaning procedures, LEIS and X-ray photoelectron spectroscopy (XPS) survey spectra were obtained. It was obvious that during cleaning bulk impurities present in the foils at a ppm-level continuously segregated to the surface.

Due to a significant contamination of $Pt_3Zr(0001)$ by graphitic carbon, an ultrathin ZrO_2 film could not be grown – despite multiple attempts and optimisation. LEIS results obtained after short sputtering demonstrated a modified surface stoichiometry (Pt/Zr ≈ 5:1 instead of 3:1). Depth profile analysis by angle-resolved XPS, performed after two different pre-treatments, indicated that the desired stoichiometry was only present in the bulk. Upon annealing, carbon, most likely located at interstitials, segregated to the surface. It is assumed that the origin of the carbon impurity within the single crystal is related to its synthesis.

CONCLUSION

Experimental results demonstrate the outstanding surface sensitivity of LEIS, especially in comparison to XPS which is also known for its high sensitivity. Furthermore, it is shown that LEIS is a suitable tool for observing the segregation of bulk impurities which has a significant impact on sample preparation and catalytic activity. The implementation of LEIS in our UHV setup was successful. Yet, there is still room for improvement which will be part of further studies.

ACKNOWLEDGMENTS

This work was supported by the Austrian Science Fund (FWF) within the SFB F45 “FOXSI”.

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TAILOR-MADE POLYMER INTERFACES – SURFACES ON DEMAND

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INTRODUCTION

The design and creation of particular interfaces between substrate surfaces and biomolecules became very attractive for research purposes and applications in the biomedical field[1]. The concept of building interfaces can be used for the manufacturing of biosensing platforms[2] (Figure 1), cell culturing, tissue engineering[3] and other fields, like cell research. In the last-mentioned area, applying the proper interface can yield profound information about the investigated species. A method for the design of such interfaces is the coating with functionalized polymer chains and covalently attached to a substrates surface, these organic linker molecules are then usually called polymer-brushes. To create such polymer interfaces, reversible addition-fragmentation chain transfer polymerization (RAFT) can be applied and the advantages of this polymerization technique are well defined polymers referring to the molecular weight or chain length distribution and a broad spectrum of compatible monomers[4] which gives the polymer chains particular properties. Custom end-groups can be introduced via application of the right chemical processes[5] and all these options make RAFT polymerization a powerful tool in the creation of custom-built complex architectures[6] with the desired chemical properties for biomedical applications[7].

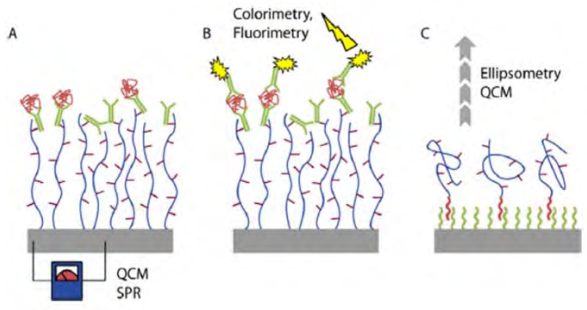

Figure 1: Biosensing platforms as an example of using polymer brushes[1]

OBJECTIVE

The aim of this project is the generation and characterization of polymer brush coatings on substrates used for cell interaction studies and tissue engineering. By application of grafting-from RAFT polymerization, 2D nano-architectures will be implemented, and in combination with photo-polymerization techniques even 3D architectures will be realized. In addition, the chemical properties of the polymer brushes will be tuned by variation of the used monomer, and the end-group functionality is easily customized via simple chemical reactions with potential for biofunctionalization (Figure 2).

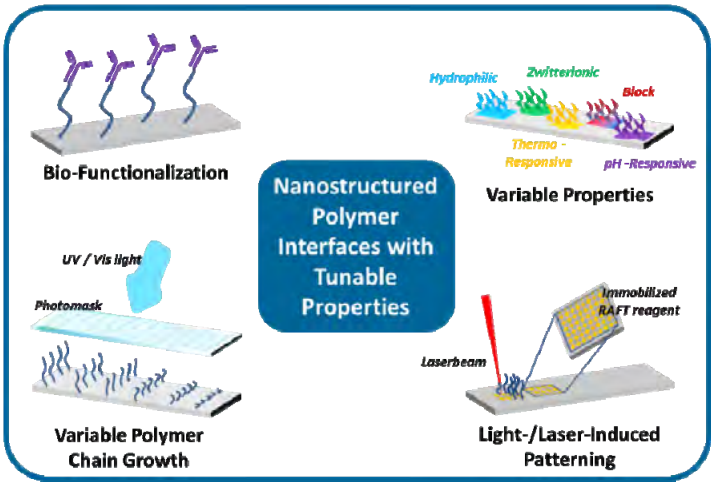

Figure 2: Potential of polymer brush coatings prepared by grafting-from RAFT polymerization

RESULTS AND DISCUSSION

The main strategy (Figure 3) involves the immobilization of a RAFT reagent on the surface, by covalent bonding. From this point a monomer is chosen to introduce the chemical properties, such as hydrophilicity, thermo-responsivity or zwitterionicity. To find the right chemical identity of such polymer brush coatings is still challenging, for applications in the presence of cells and especially the study of their interaction with such interfaces, since the coating should mimic the extracellular matrix. First results on silicon oxide substrates (Silicon wafers, glass) were achieved by the application of a trithiocarbonyl based RAFT reagent in combination with N-acryloylmorpholine (NAM), a hydrophilic monomer. Therefore, the substrate was amino-functionalized via chemical vapor deposition in step 1 and the RAFT reagent was covalently attached via N-hydroxysuccimide coupling in step 2. Most important, the grafting-from RAFT polymerization of NAM in step 3 and the end group formation to a thiol group in step 4. The polymerization step was performed via thermal initiation but also the first successful results for photoinitiated systems were achieved. All these functionalization processes were monitored via water contact angle and ellipsometry and the changes are well recognizable in every step (Figure 4). Thiol-end-groups could be detected via labeling with fluorophores and analysis by total internal reflection fluorescence microscopy.

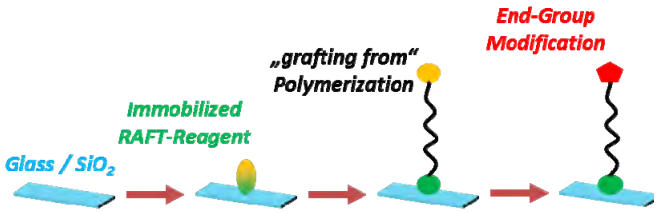

Figure 3: Step-by-step strategy for the preparation of RAFT polymer brush coatings on silicon oxide substrates

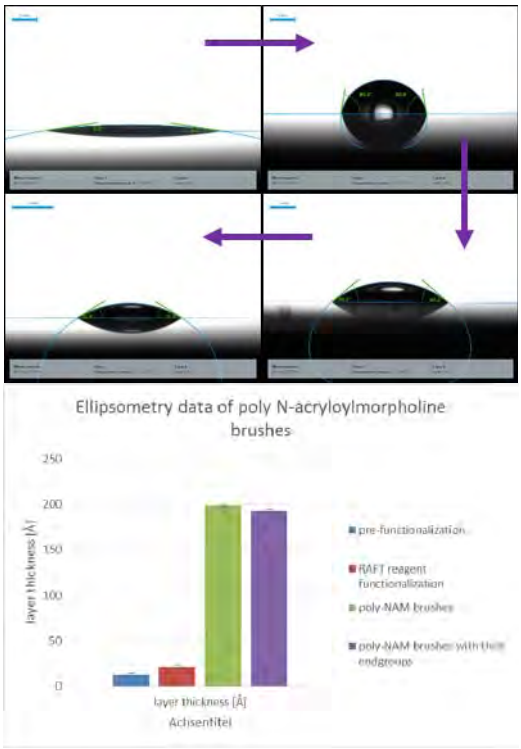

Figure 4: Contact angle measurements (top); Ellipsometry data (bottom) of a poly-NAM brush system

CONCLUSION

It was possible to apply grafting-from RAFT polymerization using NAM as monomer to coat silicon oxide substrates. By combination of the developed techniques, 2D materials with well defined architectures, chemical properties and biofunctionality for unique cell research can be established.

ACKNOLEDGEMENTS

Special thanks for funding to the doctoral school of BioInterface, TU Wien

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MODIFICATION OF PRECERAMIC POLYMERS AND INVESTIGATION OF THEIR POROSITY DEVELOPMENT

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INTRODUCTION

Porous ceramics are essential components in different challenging applications. Due to their unique properties such as low density, high permeability, high thermal shock resistance and high chemical stability, they are used in a wide field of applications, including filtration, absorption, membranes (e.g. for hydrogen separation) or light weight structural materials.[1]

The production of microporous ceramics from preceramic polymers has gained increasing scientific interest in the recent past. The main reasons are that the production of polymer-derived ceramics (PDCs) can be achieved with processing techniques not accomplishable with traditional powder technology.[2] On the other hand, significantly reduced synthesis temperatures and the lowered energy consumption make the PDC route a matter of economical and ecological interest.[3]

The objective of this work is to get a better understanding of how the presence of different organic groups in the preceramic polymer influences the resulting micropore structure during the thermal polymer-to-ceramic conversion process. For this purpose, a preceramic polymer is modified by nucleophilic substitution using different alkyl bromides as substituents.

EXPERIMENTAL PROCEDURE

In a first step a polyvinylsilazane (Durazane 1800, durXtreme GmbH, Germany) was modified by nucleophilic substitution, bringing organic groups of different size into the structure of the polymer (Fig. 1). The addition of Hünig's base (N,N-Diisopropylethylamine) prevents side-reactions by building a quaternary ammonium salt with hydrogen bromide.

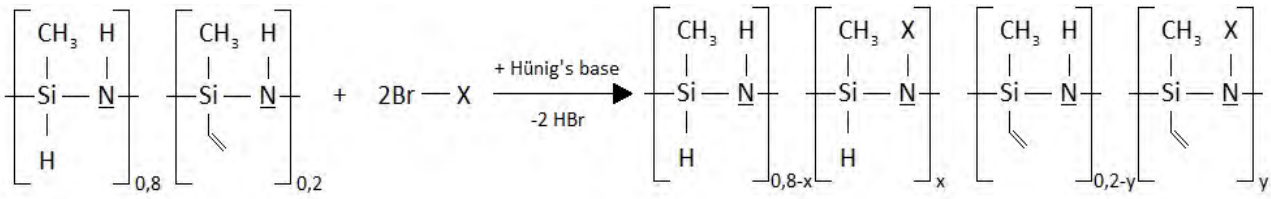

Fig. 1 Modification of a commercially available poly(vinyl)silazane by nucleophilic substitution

In a second step the modified polymer was heated under nitrogen atmosphere up to 250 °C, which results in the formation of cross-links between the polymer chains due to the presence of vinyl moieties. Cross-linking takes place without addition of further reagents, although the formation temperature can be lowered through addition of a radical initiator (e.g. dicumyl peroxide[4]).

In a final step the cross-linked polymer was heated under nitrogen atmosphere up to 600 °C. This leads to a polymer-to-ceramic conversion process, including chemical decomposition and molecular rearrangement processes, resulting in a microporous ceramic.

Structure and composition of the educts, products and of all occurring intermediate products (e.g. the modified polymers) were characterized using a variety of analysis methods, including elemental analysis, NMR and FTIR. The pore structure and the specific surface area of the produced ceramics were analyzed using N_2-physisorption.

RESULTS AND DISCUSSION

Modification of the poly(vinyl)silazane compound by nucleophilic substitution was successful for a variety of substituents. By employing a pyrolytic conversion treatment, these materials could successfully be converted into microporous materials. N_2-physisorption measurements (Fig. 2) indicate that the pore width of the produced ceramics is around one nanometer. The pore width does not appear to correlate with the size of the attached groups, possibly due to molecular rearrangement processes. The measured BET surface areas were between 220 and 235 m^2/g, significantly higher than the BET surface area of the ceramics received from the unmodified polymer. These first results are a major step towards the development of novel microporous materials, suitable e.g. for membrane applications.

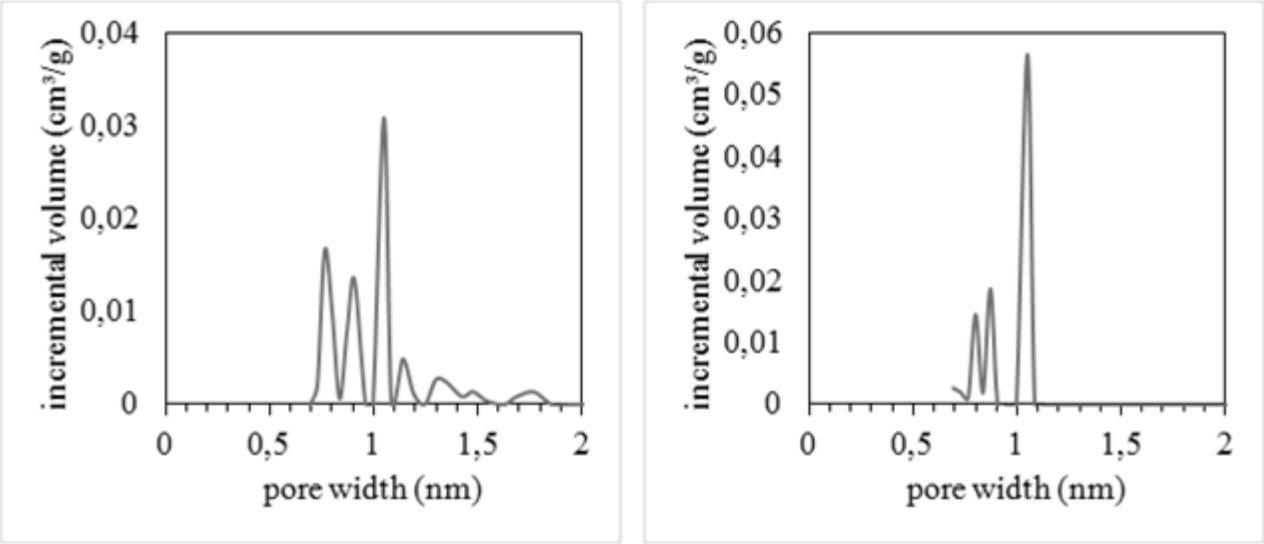

Fig. 2 Pore width distributions obtained by NLDFT analysis of N_2-physisoption data (used substituents: left: 1-Bromobutane, right: α-Bromo-p-xylene)

CONCLUSIONS

Novel nanoporous compounds could be generated by pyrolytic conversion of modified preceramic polymers based on polysilazanes. Analysis by N_2-physisorption shows that the modification of the preceramic polymer leads to pore structures in the size range of 1 nm in the final product. However, further work is required in order to understand how the resulting microporosity can be tailored.

ACKNOWLEDGMENTS

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COATING OF TUBULAR SILICON NITRIDE SUPPORT STRUCTURES WITH POLYMER DERIVED CERAMIC MEMBRANE LAYERS

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INTRODUCTION

Non-oxide ceramic membranes boast chemical and thermal stability which makes them suitable for the use in many of today's membrane processes. Because of highly beneficial mechanical and thermochemical properties, porous silicon nitride[1],[2] in combination with polymer derived SiCN [3] can be used as membrane materials, suitable for prospective uses under harsh circumstances that common polymer- or metal-based membranes cannot withstand.

The objective of this work is the development of a processing routine for preparing asymmetric membrane structures, using tubular macroporous silicon nitride supports in combination with polymer derived Si(CN) membrane layers deposited via a dip coating process similar to what Konegger et al. have described [4]. The final layer needs to be microporous (pore diameter smaller than 2 nm). Porosity can be achieved by different processes. For the macroporous support a partial sintering route was chosen, the viability of which has been demonstrated previously [5], while the microporous separation layer is produced by pyrolysis of a preceramic polymer.

EXPERIMENTAL PROCEDURE

In this work, two different coating approaches were evaluated. The first approach included an application of a mesoporous intermediate layer onto the substrate before coating it with the separation layer, while the second approach involved the direct deposition of the separation layer onto the supports.

Preparation of support structures: The tubular macroporous support structures were infiltrated with polystyrene solution (25 wt% PS in toluene) by a dip-coating process. Subsequently, the surface of the masked support tubes was polished in order to remove coating flaws.

Deposition of the intermediate layer: An intermediate layer was prepared by dip-coating the masked support structures in dispersions consisting of an organic solvent (primarily n-hexane, which does not dissolve the masking compound and does not react with the preceramic polymer), silicon nitride (SN-E10, UBE) and poly(vinyl)silazane (Durazane 1800, durXtreme GmbH). Here, the poly(vinyl)silazane compound serves as a binder. After dip-coating, the samples were crosslinked in a furnace at 130 °C under flowing nitrogen. The masking compound was dissolved in toluene before the samples were pyrolysed at 600 °C under flowing nitrogen.

Deposition of the top layer: The separation layer was either coated onto the intermediate layer or directly coated onto the masked supports by the same dip-coating procedure as before, using a solution of the preceramic polymer in an organic solvent. After crosslinking (130 °C, nitrogen) the masking compound was dissolved in toluene and the sample was pyrolysed (600 °C, nitrogen).

RESULTS AND DISCUSSION

As no stable dispersions of polymer, silicon nitride powder and compatible organic solvents could be prepared, the dispersion had to be continually stirred, which makes predicting coating behavior challenging, due to it not being a stable system. In spite of these challenges, continuous intermediate layers were successfully deposited onto the masked support structures.

An almost defect free top layer was achieved by direct coating of the masked supports (Figure 1). The number of deposition defects can be reduced by multiple coating runs. However, many variables have to be considered during the whole production process, which can influence the quality of the top layer.

Coating onto the intermediate layer appears more promising, since the surface of the layer is smoother and more homogenous than that of the support. However, development of the coating process has to be continued in order to obtain surface qualities suitable for membrane applications.

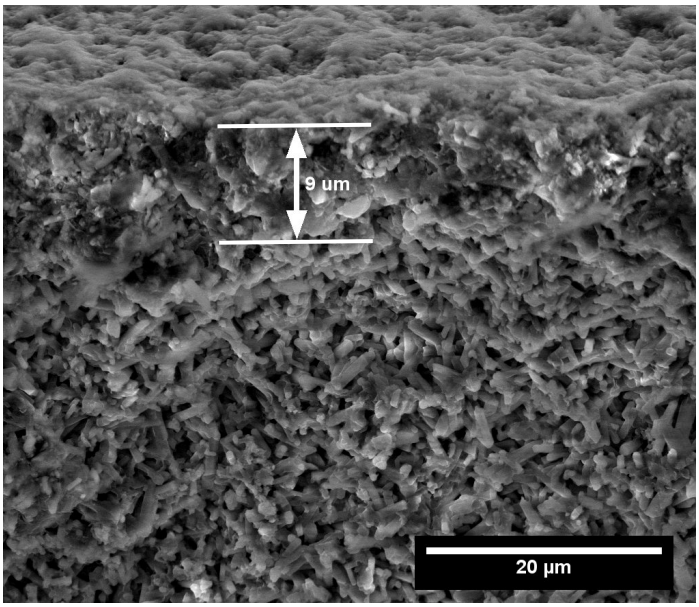

Figure 1: SEM micrograph of top layer surface after a singular coating step directly onto the masked substrate surface.

CONCLUSIONS

The coating of macroporous silicon nitride support structures with a polymer derived SiCN membrane layer of a few µm thickness was achieved using a dip coating process. An optimized masking technique allowed for a direct coating of the supports, yielding an almost crack-free top layer. An improvement of the surface quality of the substrate was achieved by adding an additional intermediate layer to the process. The results are promising and therefore, the focus lies on further continuing the deposition process development.

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FUNCTIONALIZATION OF SUPPORTED Au_{11} NANOCLUSTERS THROUGH LIGAND EXCHANGE AND COMPARISON TO LIQUID PHASE REACTIONS

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INTRODUCTION

The properties of ligand protected Au nanoclusters are known to depend on both the size and composition of their metal core [1], as well as on the nature of the surrounding ligands. This allows to synthesize clusters with various polarities or solubilities, and also different activity in catalytic reactions [2]. Therefore, tuning of cluster catalysts can be achieved by modifying their ligand shell in so called ligand exchange reactions [3].

Although these reactions have been studied widely in the last years, their application has so far been limited to free clusters in solution. For heterogeneous catalytic applications of Au nanoclusters, they are usually immobilized on powder materials, as these catalysts exhibit significantly higher stability and enhanced activity [4]. However, the possibility of introducing new ligands onto supported clusters and therefore, modifying their properties, has not been evaluated so far.

EXPERIMENTAL

In order to investigate the ligand exchange behavior of already immobilized Au nanoclusters for the first time, ligand exchange of $Au_{11}(PPh_3)_7Cl_3$ (Figure 1) with monodentate thiol ligands was chosen as a model reaction. This specific reaction is well studied in liquid phase and known to lead to either partially or fully ligand exchanged Au_{25} clusters (depending on the thiol used) [5,6]. Moreover, it allows easier investigation of the reaction outcome due to different elements (P and Cl vs. S) coordinating to the Au core prior to and after ligand exchange.

For our experiments, $Au_{11}(PPh_3)_7Cl_3$ was synthesized with modifications to previous procedures [6]. The clusters were subsequently deposited on surfaces (Al_2O_3 and ZnSe) as dropcast films or impregnated on oxide powders (SiO_2 and Al_2O_3). These samples of immobilized clusters were then exposed to solutions of the exchange ligand. Both *in-* and *ex-situ* characterization was performed, using several spectroscopic techniques (UV-Vis, IR, PM-IRRAS, NMR, XPS, MS). For the powder samples, element specific analysis was done with ICP-OES, allowing determination of the degree of exchange.

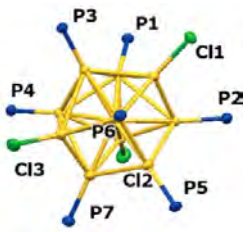

Figure 1: $Au_{11}(PPh_3)_7Cl_3$ [6]

RESULTS AND DISCUSSION

The supported $Au_{11}(PPh_3)_7Cl_3$ showed very different behavior in the ligand exchange reactions compared to free clusters. For the cluster dropcast films on planar surfaces, which were monitored with PM-IRRAS (Figure 2) and ATR-IR, incomplete exchange was noticed. This was indicated by additional bands appearing in the spectra with reaction progress, which could be assigned to characteristic vibrations of the incoming thiol ligand. The MALDI-MS spectra recorded of the products demonstrated that the number of Au atoms in the core remained constant throughout the reaction. This is a

significant difference to ligand exchange in solution, where a growth to Au_{25} was evidenced.

For $Au_{11}(PPh_3)_7Cl_3$ supported on oxide powders, a clear change in sample color and UV-Vis absorption features indicated structural changes upon ligand exchange. As suggested by HAADF-STEM, the core size was again maintained, and ICP-OES measurements indicated incomplete exchange. These results are in good agreement with those of the dropcast films and further affirm the substantial differences between free clusters in solution and immobilized clusters on support materials. It is assumed that the interaction between the Au nanoclusters and the substrate has distinct influence on their ligand exchange activity, resulting in different products.

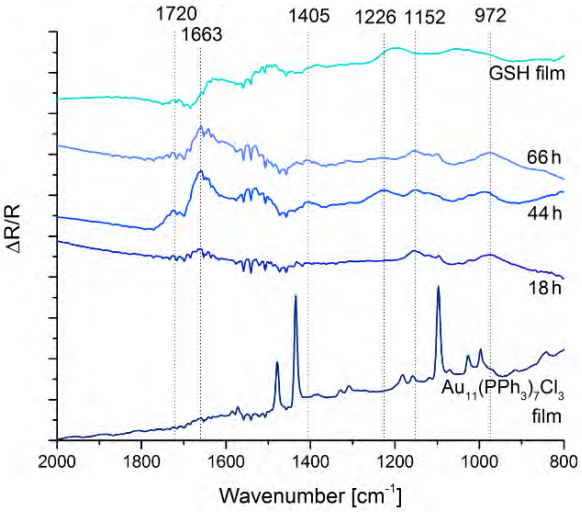

Figure 2: PM-IRRAS spectra recorded over the duration of the ligand exchange reaction.

CONCLUSION

Au nanoclusters supported on powders with high surface area are interesting candidates for catalytic activity studies. In this work, the possibility of post-functionalization of already immobilized clusters by ligand exchange was confirmed. As this allows to selectively modify the properties of nanocluster catalysts, it is likely to find broad application. In addition, it could be shown that the product of the ligand exchange with free clusters in solution versus supported clusters is significantly different.

Further studies of ligand exchanges with immobilized clusters will be performed to gain more insight into the bonding motive between cluster and substrate and the role of the ligands within that. In addition, chiral exchange ligands will be used in a next step, leading to chiral cluster catalysts.

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DESIGN OF NON-SPHERICAL COLLOIDAL POLYMER PARTICLES FOR SELF-ASSEMBLED MATERIALS

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INTRODUCTION

Self-assembly (SA) is the process by which complex aggregates are generated from the non-covalent interplay of their building blocks without any human intervention. From DNA, micelles, liquid crystalline phases or nanoparticle assemblies, a plethora of structures is generated by SA. Therefore, SA constitutes a most useful tool for synthesizing new and intriguing functional materials across various size scales. By exploiting SA, one can obtain properties that are yet to be achieved by conventional top-down or bottom-up approaches [1].

EXPERIMENTAL PART

Research aiming at generating new materials has until recently mainly been dominated by materials design on the molecular level, *i.e.* by using tailor-made molecular building blocks. One recent and highly promising route towards new materials, and therefore also novel materials properties, is to use building blocks that are bigger than molecules, *i.e.* colloidal particles, for obtaining nano- and micro-structured materials. The generation of such materials is often achieved by bringing the colloidal particles together by means of SA. Generally, SA depends on three main factors (Fig. 1A), namely: (*i*) shape, (*ii*) dimension, and (*iii*) chemical composition of the building blocks.

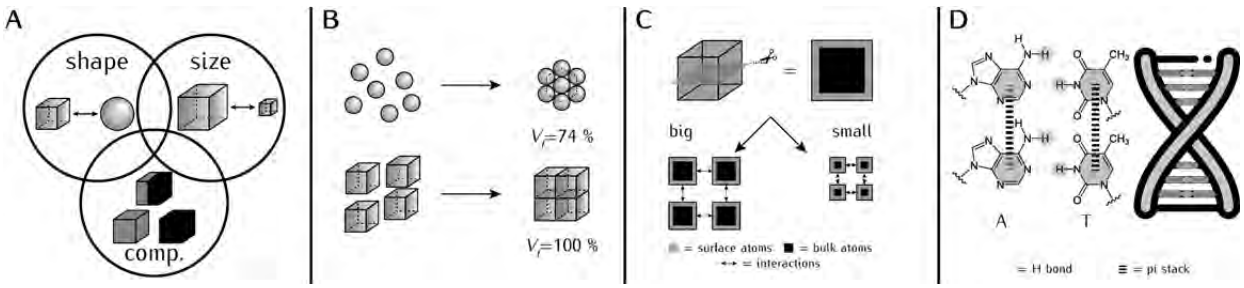

Figure 1: A - The three key parameters driving SA: shape, size and chemical composition. B - Shape determines the packing efficiency: Cubes (V_f = 100 %) can fill space more efficiently than spheres (V_f = 74%). C - Interparticle forces scale with particle size: Smaller particles have a higher surface atom/bulk atom ratio than bigger particles, leading to higher G_i. D - The DNA double helix structure arises from the interplay of π-stacking and H-bonding between nucleobases.

Shape affects the packing efficiency. For instance, spheres are able to fill up a given volume to a maximum of 74 % (closest packing), whereas cubes can fill up to 100 % of the volume (Fig. 1B). The size of the building blocks dictates their total interface free energy (G_i), therefore determining the strength of interparticle interactions (Fig. 1C). Finally, the chemical composition is responsible for the nature of cooperative interactions of the assembly. For example, H-bonding and π-stacking between nucleobases determine the double-helix structure of DNA (Fig. 1D).

Our group has recently introduced a new method towards the synthesis of anisotropic angular polyimide (PI) particles by means of solid-state polymerization (SSP) [2]. SSP is a solvent-free polymerization technique that involves heat treatment of monomer salts at temperatures below their melting point. Such monomer salts are obtained by a simple acid-base reaction between the co-

monomers diamine and tetracarboxylic acid (Fig. 2). Using monomer salts as starting materials presents some advantages over monomers used in classical syntheses: (*i*) they are single-source precursors providing ideal stoichiometry; (*ii*) they show high reactivity for the proximity of reacting groups within the salt structure; and (*iii*) they show better stability and therefore storability than the pristine co-monomers. Interestingly, for the vast majority of reported examples, SSP of monomer salts results in PI particles that retain the morphology of the initial monomer salt. Therefore, the reaction provides a promising route towards non-spherical PI particles. This project aims at modifying the dimensions and crystal habit of monomer salts in order to generate arrays of colloidal PI particles with different non-spherical shapes, and study their SA.

RESULTS AND DISCUSSION

In order to modify their crystal habit, monomer salt precipitation has been performed in presence of additives. This technique is well known in the field of crystal growth, and relies on the interaction of additives with crystal facets. By attaching to facets with higher G_i, *i.e.* with higher growth rates, additives inhibit the growth in certain directions, thus generating crystals with altered habit. With this contribution we present our investigation of (*i*) the influence of additives and (*ii*) the effect of various parameters, *e.g.* temperature or concentration, on the monomer salt formation. Specifically, we studied the monomer salt [$H_2PDA^{2+}PMA^{2-}$], obtained by acid-base reaction of *p*-phenylene diamine (PDA) and pyromellitic acid (PMA). All studied systems were characterized using optical microscopy, scanning electron microscopy (SEM), infrared (IR) spectroscopy, and powder X-Ray diffraction (PXRD). Our studies show, that it is indeed possible to alter the crystal habit of the prototypical monomer salt [$H_2PDA^{2+}PMA^{2-}$].

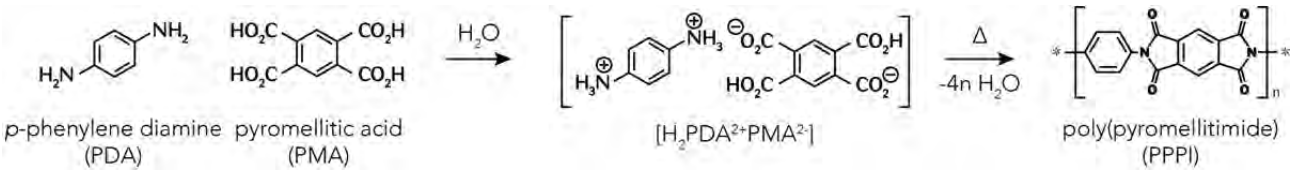

Figure 2: Acid-base reaction between pyromellitic acid (PMA) and *p*-phenylenediamine (PDA) in aqueous solution generates the monomer salt [$H_2PDA^{2+}PMA^{2-}$], which is then converted to poly(*p*-phenylene pyromellitimide) (PPPI) by SSP.

CONCLUSION

Solid-state polymerization of the monomer salt [$H_2PDA^{2+}PMA^{2-}$] is a promising route towards non-spherical polymer particles. These particles are intended to be used as particle building blocks for novel nano- and microstructured materials. In order to generate such materials and comprehensively study their formation, we aim at accessing different particle shapes and sizes at same chemical composition. For obtaining PI particles of different shape and size, we target morphology alterations at the monomer salt level. Therefore, the effect of several parameters on the obtained monomer salt form and size has been studied. Overall, it can be stated that materials generated from self-assembled particles are likely to exhibit intriguing novel properties. As PIs intrinsically display properties such as high thermal and chemical resistance, SA products of PI particles bear the potential to be promising colloidal structured high-performance materials.

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ADSORPTION OF CO_2 ON ACTIVATED LIGNITE

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INTRODUCTION

Power generation in Poland relies mostly on coal, hence extensive research efforts are now being made to reduce CO2 emissions. One of the available solutions involves gas trapping by adsorption. This study summarises the research efforts to develop a cheap and effective adsorbent based on carbon dioxide-activated lignite. Testing was done on a lignite sample from one of the Polish collieries.

EXPERIMENTS

To evaluate the quality of thus obtained sorbent, adsorption tests were performed in the laboratory conditions, involving the measurement of CO2 adsorption isotherm at 273 K. Low- pressure sorption measurements were taken with an automatic apparatus Micrometrics ASAP 2010 (Accelerated Surface Area and Porosimetry System) using the volumetric method. Formal description of experimental data relied on the Dubinin and Radushkiewicz (DR) isotherm equation, which is applicable to analyses of microporous media adsorption. The pore width distribution was derived from the adsorption isotherm by the DTF and Monte Carlo method. Results are compiled in table 1 and 2.

RESULTS AND DISCUSSION

Table 1. Analysis of DR isotherm

	Correlation Coefficient	Average Pore width	Micropore volume	Micropore surface area
DR metod summary	0.9998	1.226nm	0,148 cm2/g	394 m/g

Table 2. Comparison of results obtained by the DTF and Monte Carlo method

	Pore volume	Surface area	Fitting error	Pore width
Monte-Carlo method summary	0.110 cm3/g	358m2/g	0.305 %	0.524 nm
DFT method summary	0.114 cm3/g	387m2/g	0.425 %	0.548 nm

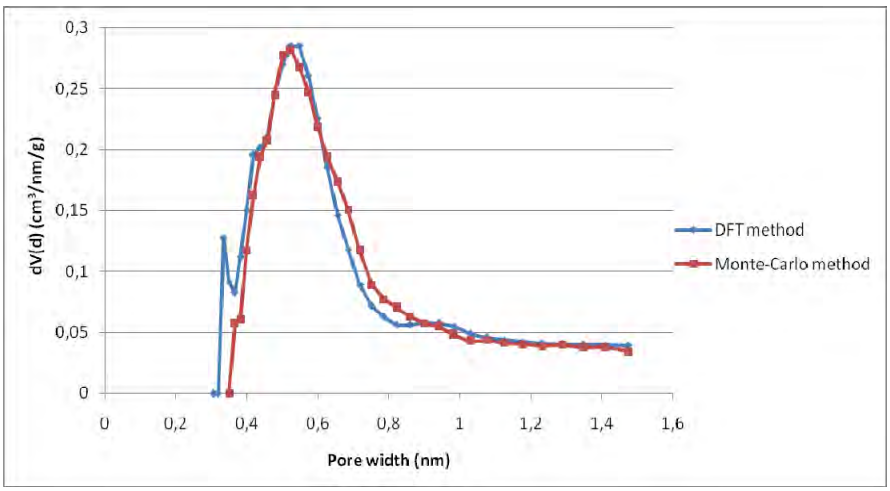

Fig 1. Pore width distribution obtained by DTF and Monte Carlo method

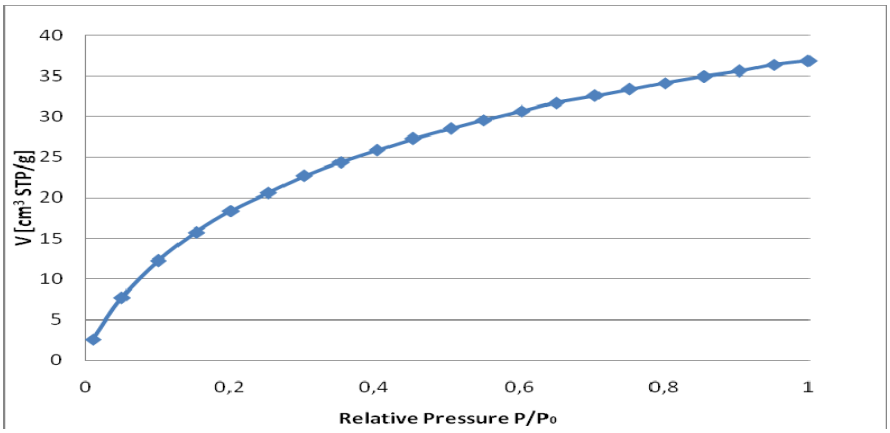

Fig 2. Isotherms of CO2 adsorption on activated lignite

It appears that thus obtained absorbent features a relatively high specific area. Good fit obtained for the DR isotherm (correlation coefficient 0.99) suggests that the absorbent structure is dominated by micropores, which is corroborated by results of DTF and Monte Carlo analysis showing that the predominant pore diameter slightly exceeds 0.5 nm (in the sub-micropore range). Comparison of results obtained by the two methods reveals the good agreement of the pore volume data and specific areas (table 2). Comparing the specific surface areas derived from the DR equation and computed by the DFT and Monte Carlo methods, it is reasonable to conclude that specific surface areas are associated mostly with the presence of micropores (<5 nm according to IUAPC classification) in the pore structure.

CONCLUSION

Results of CO2 adsorption in thus obtained carbon material are similar to those obtained in an analogous experiment performed on another lignite type (Baran et al., 2015, 2016). Experimental results clearly indicate that a simple process of physical activation of lignite will yield an absorbent with favourable structural parameters.

OBTAINING A LIGNITE-BASED BIOCHAR DISPLAYING ADSORPTION PROPERTIES

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INTRODUCTION

Power generation in Poland relies to a great extent on hard and brown coals as fuels. As a result, the power generation sector has become a major source of atmospheric emissions. Extensive efforts are made, therefore, to reduce the amounts of atmospheric emissions, particularly of carbon dioxide. The problem of too high emission levels can be resolved by gas trapping strategies utilising adsorption processes.

This study summarises the research efforts undertaken to obtain an inexpensive and effective absorbent of CO2. The precursor used in the process was lignite activated by physical methods. The conventional process of obtaining active carbons involves two steps: carbonisation and activation. Carbonisation prompts the formation of original porous structure which is further developed in the course of the activation process. In consideration of the fact that lignite features a large proportion of micropores, the carbonisation stage in our case was omitted and the activation using CO2 was performed directly, to avoid further loss of the precursor.

Testing was done on a brown coal (lignite) sample whose parameters are summarised in Table 1. The elemental analysis was carried out in an accredited laboratory of the Department of Solid Fuels Quality Assessment in the Central Mining Institute in Katowice, in accordance with the procedure set forth in relevant standards (Table 1).

Table 1. Parameters obtained from the element analysis

Coal sample	C^{daf} [%]	H^{daf} [%]	V^{daf} [%]	A^{a} [%]	W^{a} [%]
Turów (T)	70,2	6,00	54,06	12,3	8,3

EXPERIMENTS

A lignite sample with the grain size 0.5-1.5 mm was subjected to physical activation in a laboratory reactor, designed and engineered at the Department of Fuels and Energy AGH-UST. Schematic diagram of the reactor is shown in Fig 1. The activation procedure was carried at 850 °C for 15 minutes, with the use of CO_2. The lignite sample was placed in a steel basket, which was then lowered downward through a cylindrical pipe in the central position inside a xyloid furnace. The activating gas was admitted at the bottom of the furnace. The activation process being over, the sample was pushed upwards to the cooling zone where its temperature was reduced while it still remained in the atmosphere of activating gas which isolated the sample from air, thus preventing self-heating.

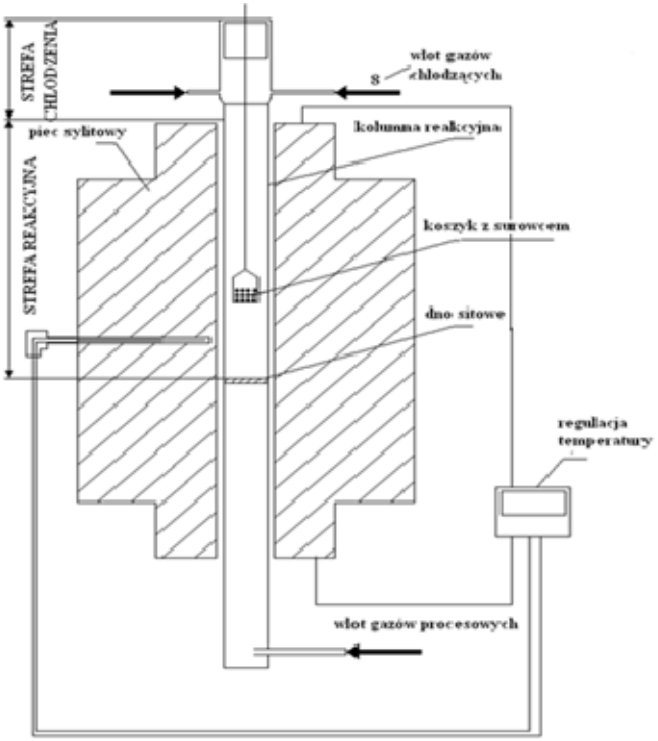

Fig 1. Schematic diagram of the reactor

RESULTS AND DISCUSSION

Experiments demonstrated a density increase following the activation process (table 2).

Table 2. Measurements of real density of the investigated lignite sample

Time [min]	0	15
Density [g/cm^3]	1,45	2,13

For thus obtained carbon material the Dubinin and Radushkiewicz (DR) adsorption isotherm equation was derived alongside the formal description of experimental sorption data. Results are summarised in table 3.

Table 3. Calculated parameters of the DR equation

Average pore width	Micropore volume	Micropore surface area
1,226 nm	0,148 cm^3/g	395 m^2/g

CONCLUSION

Application of a relatively simple method yields an absorbent with a microporous structure (the pore diameter <5 nm according to IUPAC classification) well-developed specific pore surface. Little effort was needed to obtain a valuable biochar product which can be well utilised in adsorption of carbon dioxide.

Ag_x(SR) NANOCLUSTERS SUPPORTED ON ZEOLITES AS CATALYSTS FOR ENVIRONMENTAL PROCESSES

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INTRODUCTION

Metal nanoclusters have attracted considerable attention due to their outstanding properties in comparison with the nanoparticles, tuneable at atomic scale. It open a wide range of application fields like nanoelectronics, optics, biomedicine and catalysis. In the case of catalysis, thiolate protected metal nanoclusters ($M_n(SR)_m$) open up new possibilities to create atomic precise catalytic active sites with resolved structures. A truly monodisperse catalytic surface provides ideal conditions for structure reactivity correlation studies. Extend reported studies focused on Au show that, once the cluster are supported on oxides, exhibit excellent catalytic activity in oxidation and hydrogenation reactions. It has been shown an enhancement of the catalytic properties and performance in comparison with the pair nanoparticles.

Ag and Au have contrasting physical and chemical properties despite their similarity in atomic size, structure and bulk-lattice. The difference are more accentuated going down to nanoscale and even more at nanocluster range (<100 atoms) where higher catalytic properties have been observed.(Lei, Mehmood et al. 2010) Ag clusters and nanoparticles are potentially useful catalysts in several hydrogenation and oxidation reactions. Recently,Ag_{44} nanoclusters supported on MPC show different dehydrogenation mechanism reaction with higher activity in comparison with another metals such as Pt or Pd.(Urushizaki, Kitazawa et al. 2015) This point out the opportunity for the development of novel Ag cluster catalysts.

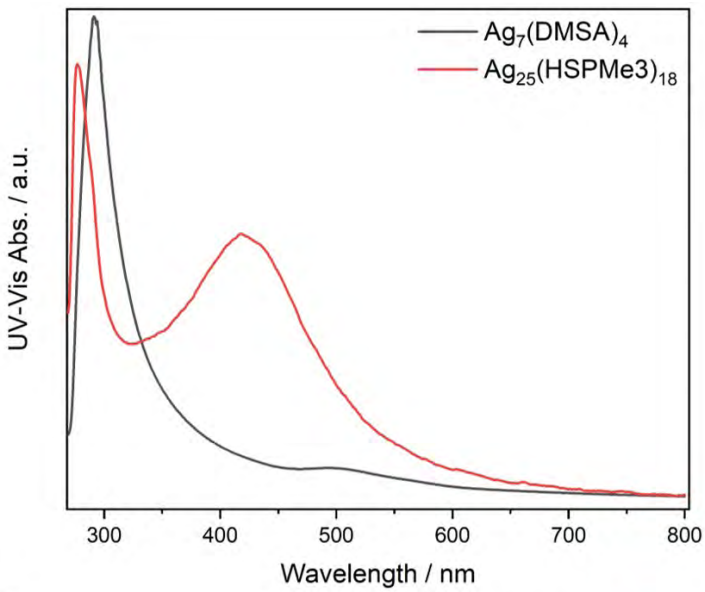
Therefore the aimof this study is the synthesis and isolation of atomically designed silver clusters, the characterization and study of their physical-chemical properties. Once the cluster are obtained, the effect of their immobilization on different kind of zeolites will be studied follow by their catalytic activity in environmental processes.

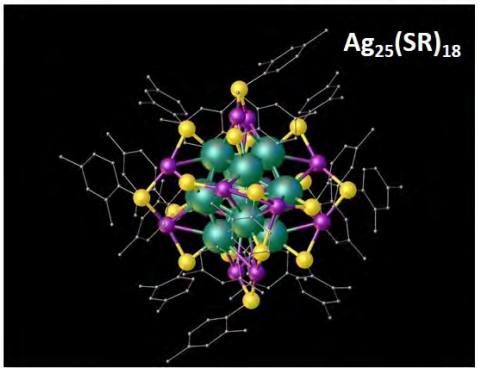
EXPERIMENTS

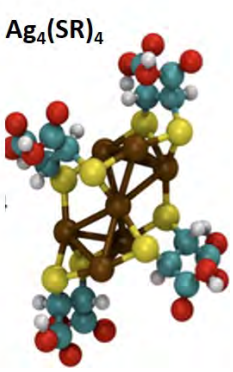
The synthesis of two different silver cluster have been performed based onBrust method [1] and previous reported works. The prepared clusters can be purified by PAGE and SEC (size exclusion chromatography). The pure Agx(SR)m clusters arecharacterized in order to know their physical-chemical properties by MALDI, UV-vis, NMR, FTIR and PL. Once the clusters are synthesized and characterized, they were immobilized in different kind of zeolites (ITQ1 and ITQ2) as supporting materials. The surface properties and his interaction with the metal will be studied by TG, FTIR-CO, XPS and TEM.

RESULTS AND DISCUSSION

The sizes of the clusters are related with the kind of thiolated ligands and the conditions of the synthesis. The first cluster synthesized was the $Ag_7(DMSA)_4$ using silver salt as precursor, DMSA as ligand and ethanol as solvent, based on reported method[2] did not lead to the expected clusters. Therefore, optimization of the synthesis protocol has been performed. The molar ratio between the precursors was adjusted as well as the times between each step. In the case of $Ag_{25}SR_{18}$, silver nitrate salt was employed as precursor, $HSPMe_3$as ligand instead of $HSPMe_2$[4] and the solvent in this case was diclorometane (DCM). UV-vis spectra of the clusters confirm the presence of the species in the samples, showing specific bands, which are characteristics for cluster Ag_7 and Ag_{25}.







CONCLUSION

To conclude several silver clusters were made with different methods of synthesis and ligands, all based on the Brust method. Optimization of the reported synthesis protocols have been made in order to obtain the desired clusters sizes. These clusters were supported in different zeolites, and their interaction and their properties are in the process of study by several techniques. Next step represents the catalytic properties study, for this the catalyst will be tested in different reactions mainly NH_3 and propane oxidation, also further studies will be performed by XAFS at synchrotron facilities (ALBA)

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STABILITY OF CATALYSTS IN SOLID OXIDE FUEL CELLS

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INTRODUCTION

Due to the increasing need for sustainable and environmentally friendly energy transport and conversion, carbon rich fuel gases in combination with Solid Oxide Fuel Cells (SOFCs) is a promising alternative.

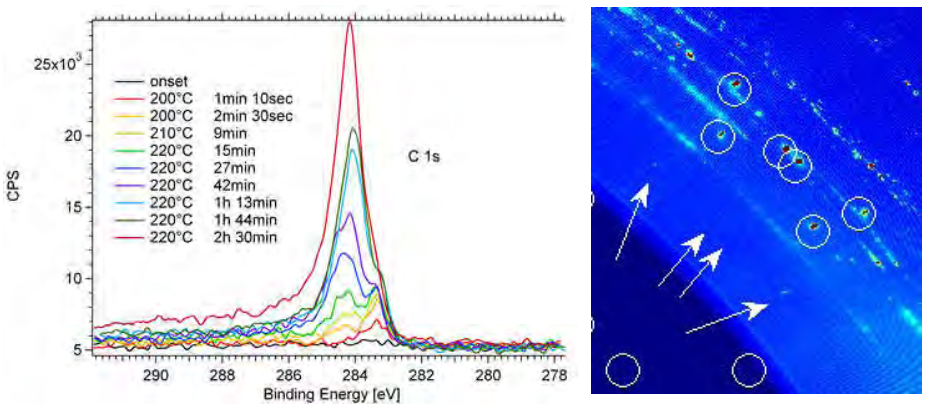
To increase reaction rates and selectivity as well as decreasing operating temperatures in SOFCs, catalysts are used. The first part presents the dynamic of Carbon on Nickel in-situ by X-ray Photoelectron Spectroscopy (XPS) and Surface X-ray Diffraction (SXRD).

The second part presents the stability of a Copper-Zinc catalyst during CO-Oxidation by ex-situ XPS and Atomic Force Microscopy (AFM).

EXPERIMENTS AND RESULTS

When SOFCs are directly exposed to e.g. Methane ($CH_4 + 2\ O_2 \rightarrow 2\ H_2O + CO_2$) the pyrolysis of Methane leads to carbon deposition, segregation and the formation of graphene/graphite as well as nanotubes on the catalyst. This can lead to deactivation (by covering active sites for the reaction) up to the mechanical destruction of the catalyst (by stress induced from nanotubes to the catalyst).

The first part of this work investigates carbon adsorption, segregation, formation and possible ways to suppress carbon formation on Nickel. In particular, the role of the clock-reconstructed on Ni(111) surface carbide regarding further C-growth and dissolution is tested and experimental data are compared to the structural models proposed in the literature[1].



Picture 1: In-situ XPS spectra of carbide and graphene/ite growth on Ni-foam(left) and SXRD of carbide on Ni(111) (right)

One main goal in understanding, improving or designing new catalysts is to pinpoint where the reaction takes place on a microscopic scale. This place is called the “active site”. Here, a clear understanding of all physical and chemical conditions coming together during the reaction is desired. This depends critically on used materials and preparation conditions as well as possible transformations during the reaction. As a first characterization, the amount of active sites on a catalytic surface is estimated by test reactions. This is used to determine the Turn Over Frequency (TOF) which quantify the reactions per site and per second. A commonly used and structural insensitive test reaction is CO- Oxidation ($2\ CO + O_2 \rightarrow 2\ CO_2$). The second part of this

work is CO- Oxidation on Zincoxide (ZnOx) supported by Copper (Cu). A comparison of the Langmuir- Hinshelwood

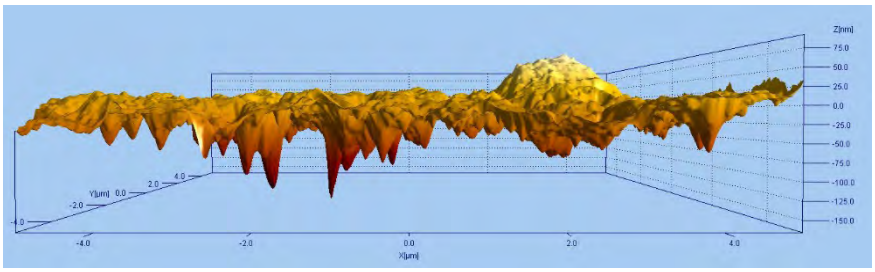


Figure 2: AFM measurements on a CuZn catalyst after CO-Oxidation. Shown is a 10x10µm area where top to bottom is 250nm. The "blob" on the right side is suspected to be a ZnOx-cluster.

Experiments were performed at the following beamlines and Ultra High Vacuum (UHV)-systems:

I. In-situ XPS at the beamline ISISS-PGM of BESSY II, Berlin

II. SXRD at the ID03 beamline of ESRF

III. Additional ex-situ experiments in UHV system, Innsbruck [2]

CONCLUSION

As shown in Fig 1, sequential formation of carbide and graphene/ite could be observed both on Ni foam and Ni (111). In addition, the coexistence of surface carbide and graphene/ite in a certain temperature region was observed as well as the preferential dissolution of the surface carbide at >= 670 K. After thermal dissolution of the carbidic clock-reconstructed $(39)^{1/2}$R16.1°x$(39)^{1/2}$R16.1°phase at 700 K, as indicated by the loss of the related diffraction intensities, the presence of epitaxial and unrotated graphene domains is indicated by the absence of rotated graphene reflections, together with a strong alteration of the specular reflectivity of the surface. These results complement recent structural investigations by Scanning Tunnelling Microscopy (STM) [3, 4]. Structure modelling of SXRD data to confirm the most plausible configurations of unrotated graphene on Ni(111) will be presented.

As shown in Fig 2, the CuZn catalyst did partake in the reaction and is structurally altered. In addition, after the first reaction cycle the catalyst did deactivate due to the strong oxidizing conditions. This shows a limitation of a classic Langmuir-Hinshelwood mechanism, where the catalyst is not changed by the reaction.

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INVESTIGATION AND RECOVERY OF FLARE GAS USING A MEMBRANE SEPARATION UNIT TO ENHANCE METHANOL SYNTHESIS PRODUCTION IN THE PRESENCE OF CATALYST DEACTIVATION

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INTRODUCTION

This research focuses on the recovery of flare gas of the world's largest methanol complex, located in Pars Special Economic Energy Zone of Iran. The work aiming at an increase of methanol production and process efficiency by utilizing flare gas components in an environmentally friendly way. Methanol is produced by the catalytic conversion of the synthesis gas over a commercial catalyst (Figure 1). Important Reactions are shown in Eq. 1-3.

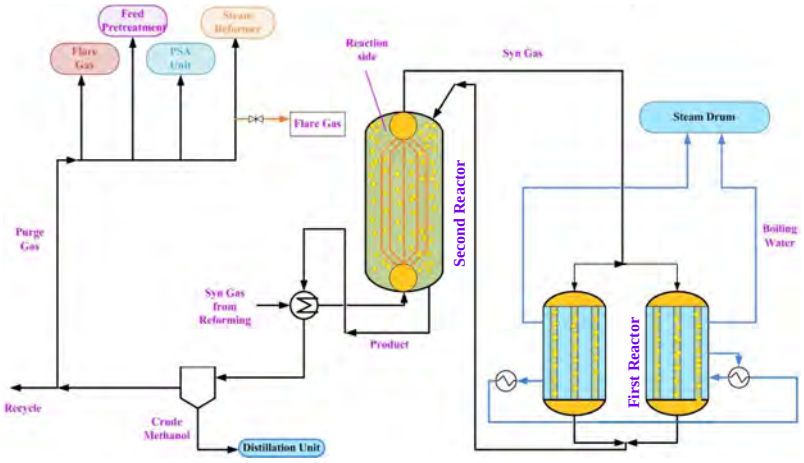

Figure 1: Schematic diagram of the methanol production unit

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{298} = -90.00\ kJ/mol \qquad \text{Eq. 1}$$
$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{298} = -49.43\ kJ/mol \qquad \text{Eq. 2}$$
$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{298} = +41.12\ kJ/mol \qquad \text{Eq. 3}$$

MATHEMATICAL MODEL

A one-dimensional steady state model has been used for this fixed-bed reactor to determine the concentration and temperature distributions inside the reactor. To obtain the mole and the energy balance equations, a differential element along the axial direction inside the reactor was considered [1-3]. The simulation of the novel process chain is shown schematically in Figure 2.

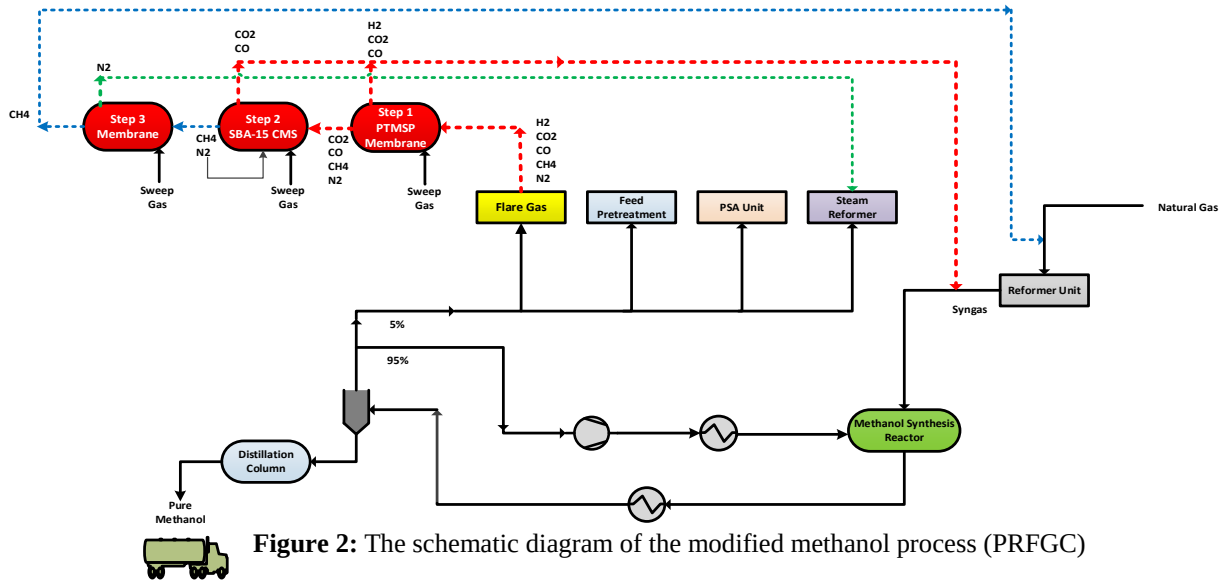

Figure 2: The schematic diagram of the modified methanol process (PRFGC)

RESULTS

The developed steady-state model was validated under industrial conditions and the results of simulation with daily-real plant data were in very good agreement. The achieved simulation results from comparison of Industrial Configuration (IC), Recycle Flare Gas Configuration (RFGC) and purposed strategy, named as Purified Recycle Flare Gas Configuration (PRFGC), are illustrated in Figure 3 & 4.

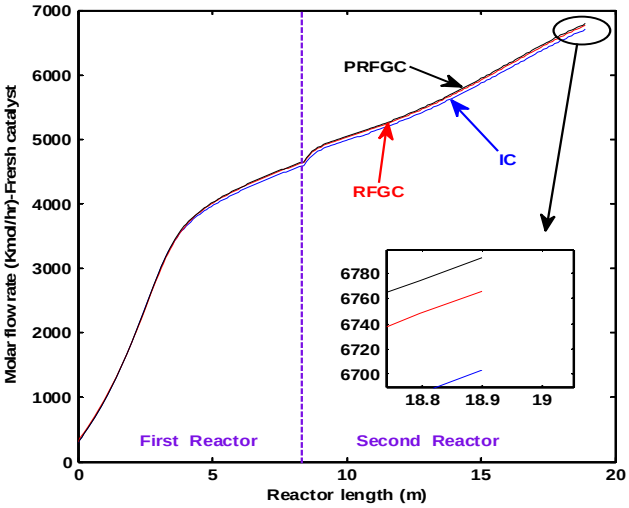

Figure 3: Methanol production along the reactor length

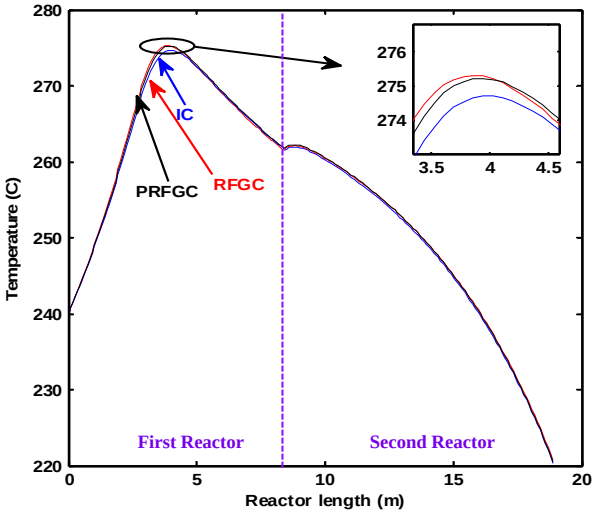

Figure 4: Temperature along the reactor length

Consequently, the methanol production rate obtained from the modified process PRFGC is significantly more than with IC. The reason of lower methanol production in RFGC in comparison with PRFGC is the inert gas increase in the reaction medium. The loss of catalyst activity, which corresponds to the loss of active surface area, is due to thermal sintering in commercial low-pressure $CuO/ZnO/AL_2O_3$ catalysts (Figure 5). The effect of specific catalyst deactivation is considered in the model.

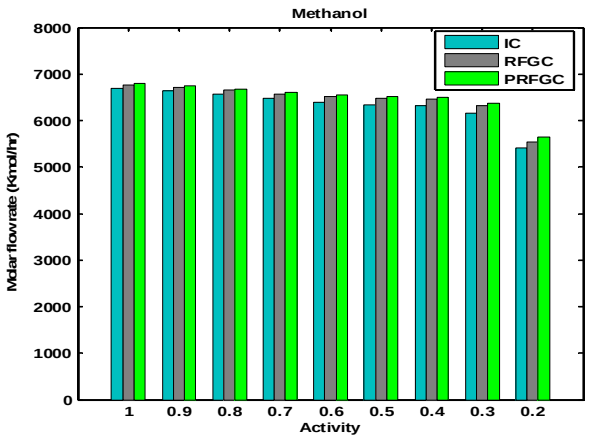

Figure 5: Influence of catalyst activity on the performance of methanol production

CONCLUSION

- A novel recovery-process is presented: PTMSP and SBA-15/CMS membranes are used to separate H_2, CO and CO_2 from the flare gas. An additional membrane separates CH_4 from N_2.
- Up to 17.3 ton/h of flare gas (60% H_2, 20% CO & CO_2, 20% N_2 & CH_4) can be reused.
- 12-14 million US-$ annual profit increase due to the increased methanol production is possible.
- With the modified process chain emission of more than 30300 ton/year of CO_2 to the atmosphere can be prevented by recovering flare gas to the methanol production process.

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DEVELOPMENT OF A TRULY HOMOGENEOUS AND MONODISPERSE CATALYTIC SYSTEM IN MEANS OF THIOLATE PROTECTED GOLD NANOCLUSTERS

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INTRODUCTION

Catalysis plays an important role in optimizing chemical processes in terms of cost efficiency and energy consumption. Further, the emission of poisonous or greenhouse gases can be reduced, leading to higher health and living standards. Catalytic processes are know for their complexity, which hampers catalysis research. New paths need to be taken to simplify reaction systems for investigations at ambient pressure. In heterogeneous catalysis metal nanoparticles are common active sites. [1] To get around the variation in particle size and size distribution of nanoparticles thiolate protected nanoclusters can be utilized.

Thiolate protected Au nanoclusters $Au_n(SR)_m$ supported on oxides have been proven to be active in several catalytic reactions with high yields. In contrast to nanoparticles, which usually have a size distribution, nanoclusters are well defined with resolved structures and offer the possibility to atomically design a truly homogenous system. This leads to optimal conditions for reaction and mechanism studies in catalytic research. Limited stability under harsher conditions has been overcome by supporting the clusters on solid materials like CeO_2. [2–5] When deposited on a support, the ligands can be successively thermally removed to expose the metal atoms and obtain a truly monodisperse heterogenous catalyst. Different activity and selectivity in catalysis were observed, depending on the atomic composition, degree of ligand removal and pre–treatment. [4–7] However, surface studies on the state of the cluster structure and ligand effects after pretreatment or during catalytic reactions have not been performed yet, but are crucial for a mechanistic understanding. The present work represents the first operando XAFS studies of monolayer protected gold cluster catalysts under pretreatment and reaction conditions. Investigations were performed with a $Au_{38}(SC_2H4Ph)_{24}/CeO_2$ catalyst in a CO oxidation model reaction. The structure of this specific cluster is shown in Figure 1.

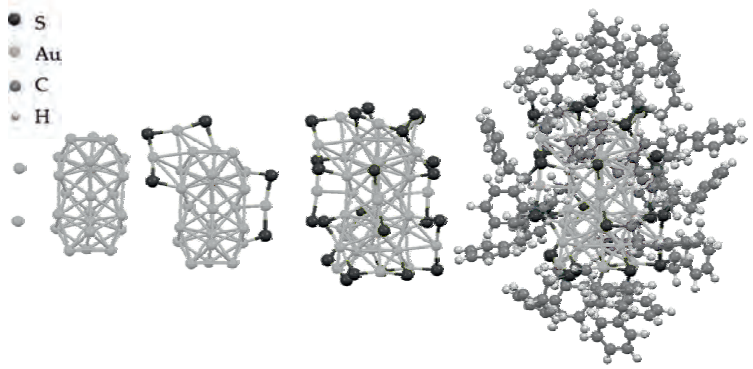

Figure 1: $Au_{38}(SC_2H_4Ph)_{24}$ nanocluster: 2 center atoms, metallic core, coordinated S–Au–S bonds, complete cluster with ligands

EXPERIMENTAL

$Au_{38}(SC_2H_4Ph)_{24}$ clusters were made by a wet synthesis approach through ligand exchange. To investigate the cluster's stability during pre–treatment and under reaction conditions, XAFS measurements were performed. At CLAESS beamline of ALBA Synchrotron, *in–situ* XANES studies at Au L_3–edge of the catalyst were performed during thermal treatment in oxidizing atmosphere and during

CO oxidation. CO conversion was followed simultaneously with MS to analyze the catalyst's activity profile. Additional *ex–situ* EXAFS at Au L_3–edge and XANES measurements at S K–edge were performed on samples pretreated under various conditions to investigate the pretreatment effect from the point of view of the ligands. Investigation of the oxidation state and particle size of the support and the deposited clusters before and after reaction were done by XPS and STEM–HAADF, respectively.

RESULTS AND DISCUSSION

The XAFS measurements represent the first evidence for a redistribution of the thiol ligands between nanoclusters and support. Further conversions of oxidation state in the S species were observed upon thermal pre–treatment, leading to different activity profiles in the model reaction. The selectivity changes in several reactions, depending on the level of ligand removal. This can be explained by the continuous evolution of new oxidized S species. [6,7] Au L_3–edge measurements point out the importance of a soft pretreatment in order to obtain a stable catalyst. The XANES spectra of the unpretreated samples during CO oxidation reaction evidence the changes of the clusters, related to modifications in both the ligand shell (Au–S) and also the remaining Au core (Au–Au). Once the samples had been pretreated, no relevant changes in the XANES spectra were observed, denoting the high stability of these catalysts.

CONCLUSION

Thus, these results obtained by XAFS, together with complementary studies (XPS, STEM–HAADF), confirm highly active and stable catalysts in form of a well defined cluster catalyst system, which are tunable by atom number, support material, different ligands and through the introduction of dopant atoms to find optimum conditions for different reactions.

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MOLECULAR DESIGN TOWARDS NOVEL PHOTO-INITIATORS WITH INCREASED TWO-PHOTON ABSORPTION CROSS SECTION

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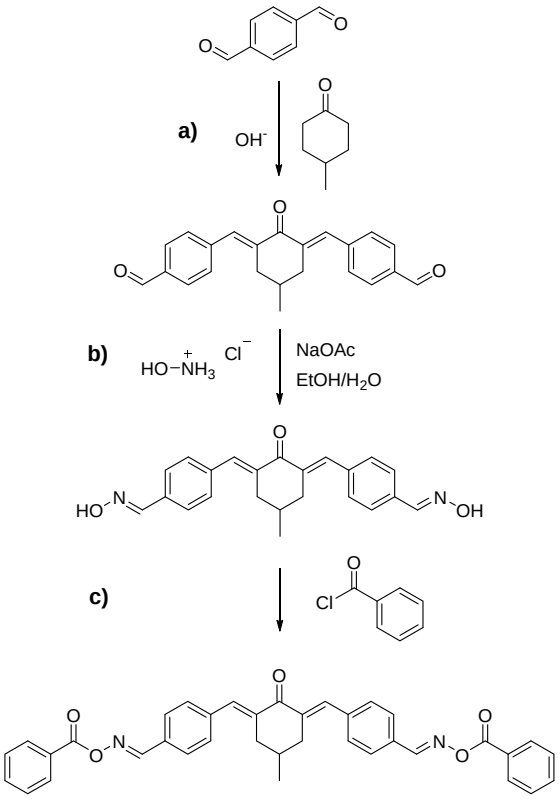
INTRODUCTION

Photopolymerization has become a valuable technique within additive manufacturing technologies (AMTs) to locally crosslink photosensitive polymers with high temporal and spatial control.[1] In order to initiate radical photopolymerization a variety of photo-initiators (PIs) are available. Two-photon polymerization (2PP) has been recently employed within the biomedical sector, since photopolymers can be crosslinked under relatively mild conditions.[2] Two-photon absorption (2PA) is a non-linear optical process, only occurring at the focal point of laser beams, where intensities are high enough for two-photon initiators (2PIs) to absorb the energy of two photons simultaneously. In contrast to one-photon absorption, where molecules are excited to an electronic state, which corresponds to the energy of one photon, 2PA is a process with rather low probability and requires extremely high laser peak powers. Due to the high transparency of biological tissues towards the pulsed infrared laser it is possible to scan the laser through a liquid formulation, enabling 3D printing in the presence of living tissue. For this process, molecules with large 2PA cross sections are needed, to ensure efficient radical polymerization. Planar and multi-polar molecules with electron donating and –withdrawing groups, as well as large delocalized π-electron systems have been known to show large 2PA cross sections. These structural properties of 2PIs have been studied to enhance polarization of molecules and their absorption properties, necessary for 2PP.[3] Continuous development of 2PIs is crucial to ensure efficient photopolymerization of new systems. There are several concepts in order to increase 2PI efficiency, such as reducing the chance of unwanted processes like back electron-transfer (BET). BET simply reverses reaction kinetics of the initiation reaction, thus decreasing 2PI activity. By the introduction of efficiently and irreversibly cleavable functional groups, such as oxime ester functionalities, BET can be minimized.[4]

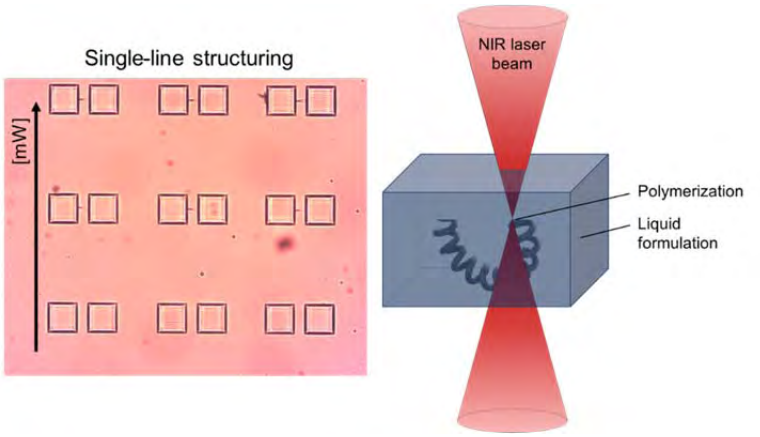


Picture 1: Synthesis of new two-photon initiators

EXPERIMENTS

Based on this concept, new cyclic ketone-based 2PIs have been synthesized according to a 3-step synthesis plan (Picture 1). Irreversibly cleavable oxime ester functionalities have been introduced

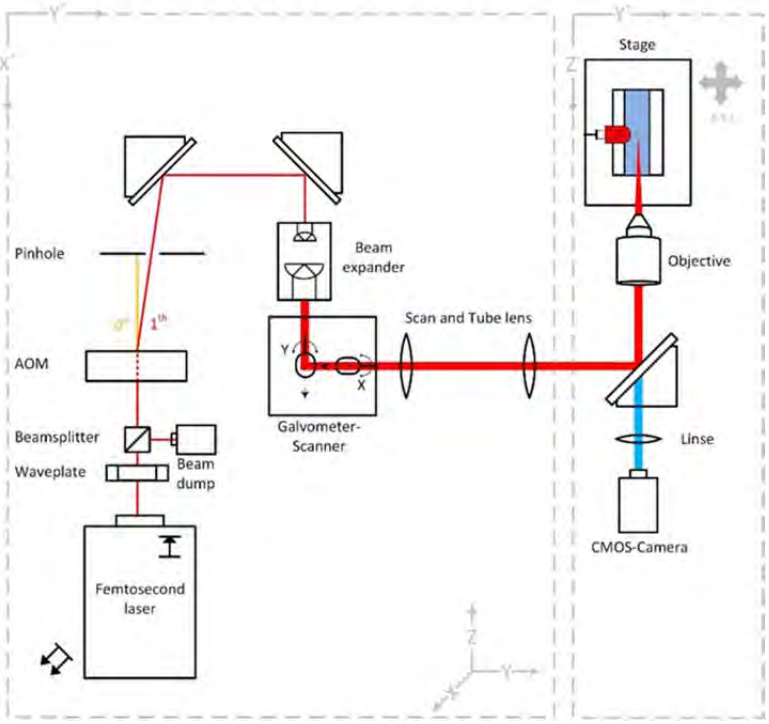
within the molecular structure by selective Claisen-Schmidt condensation of terephthalaldehyde and methyl cyclohexanone. Subsequent synthesis of aldoximes and esterification reaction with acid chlorides led to newly developed 2PIs containing oxime ester moieties. Single-line structuring tests of an acrylic resin containing 2PIs have been performed to evaluate laser power thresholds during 2PP processing (Picture 2). Furthermore, 2PA properties at varying wavelengths have been measured by a fully automatized Z-scan set-up. The experimental set-up for 2PP is depicted in Picture 3.



Picture 2: Single line structuring array of an acrylate resin to determine polymerization threshold of the formulation

RESULTS AND DISCUSSION

Accordingly, a novel 3-step synthetic approach was developed in order to design novel 2PIs. Centrosymmetric conjugated two-photon active chromophores have been developed and characterized accordingly. Single-line structuring tests have been conducted to investigate polymerization thresholds of new formulations. Selective coupling of irreversibly cleavable functional groups (oxime esters) to two-photon active sensitizers led to novel 2PIs with minimized BET.



Picture 3: 2PP set-up for the micro-fabrication of newly developed 2PIs

CONCLUSION

Molecular design towards 2PIs with increased 2PA cross sections is crucial to improve 2PP processing. Constant demand towards improved 2PI efficiency reinforces molecular development of new systems. In order to determine biocompatibility, water-soluble molecules will be synthesized and investigated accordingly. Future experiments will include cell-culture studies to investigate long-term viability of living cells in combination with novel 2PIs.

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RAFT POLYMERS AS ADHESION MOTIFS FOR BONE GLUE APPLICATIONS

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INTRODUCTION

The number of patients with minor and major accidents coming into accident and emergency care is steadily rising due to increasing life spans and the aging of our society. In order to ensure efficient care and health of human beings, medical methods need to be optimized. The fixation and adhesion between tissues, implants or scaffolds have to be refined, but the number and versatility of biomimetic and biocompatible adhesives that can be used for such purpose is limited. Up to now, adhesives based on cyanoacrylates, polyurethanes, epoxy resins or poly(methyl methacrylates) still bear several drawbacks ranging from possible allergic response, lack of mechanical strength to toxic side products. Therefore, new biomimetic glues for bonding of tissue-tissue and tissue-implant interfaces are urgently needed.

MATERIALS AND METHODS

A major challenge in determining the adhesion properties of a putative bone glue in a macroscopic setting is to distinguish between cohesive and adhesive forces. One approach circumventing this problem is to measure the adhesion via single molecule force spectroscopy (SMFS) referring to Lee *et al*.[1] This approach allows further to directly investigate adhesion processes at molecular level.

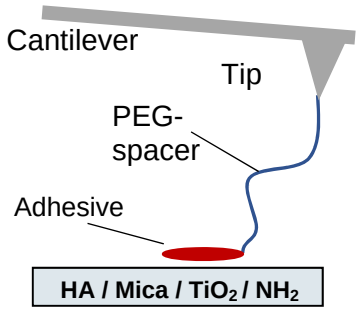

Figure 1: Adhesion measurement

Witin this study this approach was followed and a procedure was established to graft an adhesion motif onto the tip of an AFM cantilever via a linker system. In SMFS experiments the AFM tip works as a force sensor with pN resolution (see Figure 1).

In order to validate our approach, we decided to compare adhesion values with literature.[1] Therefore, the same dopamine-thiol compound as used by Lee *et al*. was attached to the AFM tip, adhesion force was measured and compared to published values. The hypothesis of this study was that the amino acid sequence D(pS)(pS)EEKC provides a strong and specific adhesion motif for hydroxyapatite, which is the organic component of bone. The specific amino acid sequence was chosen based on its suggested binding properties to hydroxyapatite in statherin[2] and due to similar sequences existing in non-collagenous proteins in bone, which are thought to be adhering to hydroxyapatite. We further hypothesised that the phosphorylated serines (pS) were largely responsible for the high interaction to Ca^{2+} in hydroxyapatite. In order to investigate this, an additional amino acid sequence with serines (not being phosphorylated) DSSEEKC was selected and tethered to an AFM tip. This allowed comparison of adhesion of the amino acid sequence with and without phosphorylation.

In the last few years studies of phosphorus-based polymers have attracted attention because of their large variety of applications.[3] In this study, we additionally investigated such polymers with regards to their adhesion properties. Therefore, we synthesized phosphor-containing methacrylates.[3] These monomers can bind to hydroxyl, carboxylic or amino groups of the organic collagen of a bone and form complexes with Ca^{2+} ions in the inorganic components. The synthesized phosphor-containing methacrylates were polymerized via reversible addition-fragmentation chain transfer (RAFT) polymerization. In this study, we prepared block copolymers with different molecular weight of dimethyl(methacryloyloxyethylmethacrylate) (DMMEP) and hydroxyethyl methacrylate (HEMA). These block-copolymers were tethered to the AFM tip and the adhesion properties were studied via single molecule force spectroscopy. The higher the amount of DMMEP (more ester groups), the higher should be the interaction between polymer and surface.

RESULTS AND DISCUSSION

In order to validate tip functionalization and experimental SFMS procedures the adhesion measurement with the linker system, the mean adhesion values of dopamine-thiol on TiO_2 were compared with literature. The measured adhesion values were in the same range as reported by Lee *et al*.[1] The pull-off forces of the naked tip were significantly lower than of the linker functionalized tip, which leads to the conclusion, that the attachment of the linker system was successful. Furthermore, the mean adhesion values of D(pS)(pS)EEKC on hydroxyapatite and TiO_2 were significantly higher compared to the values of DSSEEKC. As a result it was proved that, the phosphorylated serines were indeed responsible for the higher adhesion force on hydroxyapatite and on TiO_2 as it was suggested in literature.[2]

The synthesized block copolymers had significantly higher pull-off forces than dopamine (reference) and the amino acid sequences. The block copolymers with more polyDMMEP showed higher adhesion forces than the ones with less polyDMMEP. Thereby the phosphorus ester plays an important role to adhere on these substrates.

CONCLUSION

By the establishment of a procedure to graft a linker system with dopamine-thiol on the tip of an AFM cantilever, it was possible to measure the same pull-off forces on several substrates similar to Lee *et al*.[1] Moreover, it was proven that phosphorylated serines play a decisive role in adhering on hydroxyapatite. This means that the D(pS)(pS)EEKC motif can indeed be considered as a fully biocompatible adhesion motif for a bone glue. In addition to that, the block-copolymers with a longer block-chain of polyDMMEP showed very high adhesion especially on hydroxyapatite and TiO_2. Further research is now required at larger length scales to elucidate the feasibility of adhesives based on these motifs.

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ACKNOWLEDGEMENT

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THERMOPLASTIC POLYURETHANES AND THEIR APPLICATION AS ELECTROSPUN BIODEGRADABLE SOFT TISSUE MEDICAL PROSTHESES

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INTRODUCTION

Cardiovascular diseases are the number one cause of death worldwide.[1] Several surgical interventions are established as treatment methods with a common denominator: the necessity of medical prostheses with a wide range of demanding properties. Prostheses for soft tissues such as vascular grafts or heart valves must be biocompatible, flexible and robust to persevere blood pressure, and appropriately porous. Recent studies have shown that degradation of the artificial material enables and promotes native tissue growth. Therefore, degradability has also become a desirable attribute. Additionally, economic factors such as cost and shelf life are essential for the realization of medical prostheses.[2] Finally, it is also well known that the surface structure of medical prostheses plays a critical role in successful implantation. Segmented thermoplastic polyurethanes (TPUs) are a polymer class which meets many of the above mentioned criteria.[3] The polyaddition of diols and diisocyanates via the establishment of urethane bonds yields linear, thermoplastic polymers. Due to the urethane groups' ability to form hydrogen bonds, a segmented secondary structure can be achieved in which long, linear segments (poly(tetrahydrofuran) (pTHF) or poly(hexamethylenecarbonate) (pHMC) as soft blocks) are responsible for the material's elasticity, while the hydrogen-bonding urethane blocks from isocyanates (hexamethylenediisocyanate (HMDI), 4,4'-methylene-bis(cyclohexylisocyanate) (H_{12}MDI), 1,3-bis(iso-cyanatomethyl)cyclohexane (BIMC), or isophoronediiso-cyanate (IPDI)) and diol-chainextenders (CE: bishydroxyethyleneterephtalat (BHET), bishydroxypropane-carbonate (BHPC), or CEs from biogen substances as hard blocks) achieve mechanical stability. For the introduction of degradability of the material we aim to introduce cleavable bonds such as esters or carbonates, both in the soft and hard segments of the TPU polymer chains. Therefore, the design of cleavable chain extenders (CCE) is of special interest.

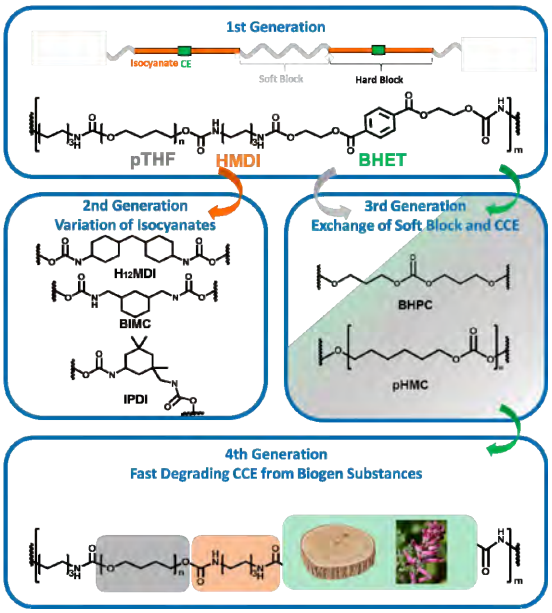

Figure 1: Schematic overview over the four TPU generations for soft tissue medical grafts

MATERIALS AND METHODS

The synthesis of linear TPUs requires the use of the prepolymer method. In order to analyze the polymers' properties, size exclusion chromatography and dynamical mechanical analysis are

conducted. Tensile testing is performed with specimens made by an optimized method for solvent casting. Biocompatibility and -degradability are tested *in vivo* and *in vitro*. Electrospinning has been chosen as processing method to create vascular grafts and heart valves from the designed TPUs because the technique provides an appropriate surface structure for such prostheses.[4] During this process a continuous polymer solution stream is converted into a nanofiber through the application of an electrical field between the tip of the syringe holding the polymer solution and a rotating rod on which the spun fiber is collected.

RESULTS AND DISCUSSION

So far, three generations of materials have been developed, a summary over the chemical composition of each TPU generation is given in figure 1.[5-7] The first generation of degradable TPUs was superior to the non-degradable commercial TPU Pellethane due to better *in vivo* vascularization of the material.[4] The design of the second generation aimed to enhance mechanical stability of the grafts by using more rigid isocyanates in the hard block. The introduction of carbonate-moieties in the third generation of TPUs decreased inflammatory responses due to less acidic, non-autocatalytic degradation. This material's enhanced mechanical properties were attributed to the introduction of carbonyl-moieties that contribute to hydrogen bonding. However, degradation speeds decreased for polycarbonate urethanes. After further optimization generations 1 and 3 have been scaled up to make vascular grafts and heart valves for *in vitro* and *in vivo* testing.[4] Currently, a fourth generation with faster degradation speed and biobased compounds is investigated. Fourth generation CCEs exhibit bonds that are prone to biodegradability and the degradation process should release the original reactants that are ideally FDA approved. In the best case, this novel cleavable chain extender concept may lead to an *in situ* long term drug-releasing biomaterial. Furthermore, these CCEs are highly rigid due to conjugation which implies high mechanical stability of resulting polymers.

CONCLUSION

The illumination of the structure-property relationship of the first three generations lead to the conclusion that moieties that contribute to hydrogen bonding (e.g. carbonyl groups) drastically ameliorate the mechanical strength of materials, also if their contribution to the material in weight percentage of the polymer is very low. Furthermore, the rigidity of hard block compounds can be detrimental to mechanical stability if they are sterically demanding due to hindrance of hydrogen bonding. With the gained knowledge about the structure-property relationship, new potential chain extenders have been synthesized and are about to be tested in polymer formulations. This will lead to a new generation of high performance artificial vascular grafts and heart valves with lower inflammation reactions and regenerative stimulus via tunable degradability to enhance long term efficiency of the prosthesis.

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MODELING ELECTRO-ACTIVE DIELECTRIC AND ELECTROSTRICTIVE ELASTOMER PLATES IN THE FRAMEWORK OF NONLINEAR STRUCTURAL ELECTRO-MECHANICS

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INTRODUCTION

One of the major innovations in the context of future smart materials is the expansion from current ceramic based materials to the usage of soft materials, e.g in view of building bioinspired soft robots. One group of smart materials, which has gained attention because of their muscular evoking behavior when subjected to an electric field, are dielectric/electrostrictive elastomer actuators. Because of their simple design- sandwiching the elastomer between two electrodes (see Figure 1), the inexpensive and easy manufacturing process and their superior performance when it comes to voltage induced deformations, these actuators are also termed artificial muscles.

Yet, practical applications suffer from a variety of failure and instability mechanisms, motivating a theoretical study on these elastomer actuators in order to help circumventing some obstacles. In this contribution, the modeling framework for electro-active dielectric and electrostricitve elastomer actuators is presented.

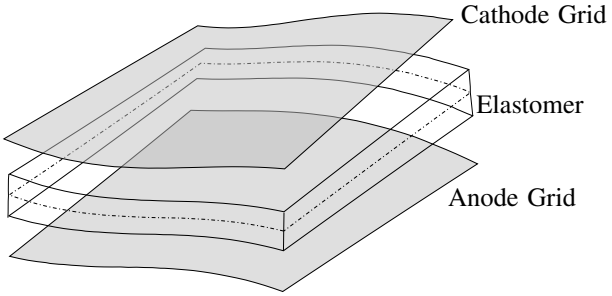

Figure 1: Construction of an electro-active elastomer actuator.

MODELING FRAMEWORK

The starting point of our derivation is a continuum mechanics framework, which allows to write the balance equations as function of electric and mechanic field quantities with regard to the whole three dimensional set-up. From the 1st law of thermodynamics, a free energy function additively decomposes of a pure mechanical, and an electrostatic energy $\Psi = \Psi_{me} + \Psi_{el}$, rendering the basis of the model. This allows for a modular incorporation of any nonlinear phenomenon crucial to the electro-elastic coupling of an electro-active elastomer actuator or sensor. The mechanical part Ψ_{me} takes the (hyper-)elastic energy of the polymer chain-network microstructure into account, while the electrostatic part Ψ_{el} features the re-orientation of dipoles upon application of an external electric field, causing a polarization and hence Coulomb-type electrostatic force- and moment couples within the elastomer.

Because of the large deformations, a geometric nonlinear formulation, where field quantities in the current configuration are referred to a reference configuration, using the deformation gradient tensor $\mathbf{F}$, is crucial. Some actuators exhibit even larger deformations because of crystalline particles embedded in the polymer network matrix. These crystalline dipoles rotate, when an external electric field is applied, and cause, independently of the applied field direction, an additional effect through the thickness of the dielectric. This so called *electrostrictive* effect, is accounted for by means of a multiplicative decomposition of the deformation gradient tensor $\mathbf{F} = \mathbf{F}_{me} \cdot \mathbf{F}_{el}$. Once all the crystal units have aligned, further deformation relies on the polymer network matrix, and polarization sat-

uration takes place. We account for this effect by incorporating a proper saturation function to the electrostatic energy Ψ_{el}, featuring relevant material properties known from experiments.

Solving for the whole set of three dimensional equations numerically might be computationally intensive and for most of the applications even unnecessary, as typical applications feature very thin designs. This encourages us to seek for solutions within the structural mechanics framework, considering plates as a material surface.

RESULTS AND DISCUSSION

To this end, the resulting three dimensional constitutive law is reduced to the structural level by applying a plane stress condition. Incompressibility of the elastomer is ensured by introducing a Lagrange multiplier, where by an appropriate decomposition of the Green-Lagrangian strain tensor a complete decomposition into a membrane free energy, and a bending energy is accomplished. This completely two dimensional energy comprises the bases for the finite element implementation into our in-house finite element code ShellFE.

Figure 2 shows the finite element results of a circular ring plate actuator, where the outer radius is clamped. Upon application of a voltage between the two electrodes on top and bottom of the circular ring, the inner circle gradually shrinks as the voltage is ramped up. A possible application might be a circular valve actuator, with the possible objective to build a biocompatible unit. Another possibility builds on a combination of multiple actuators into a matrix such that an electrically driven sieve or separator can be realized. However, yet, these ideas remain part of the future, because electro-active elastomer actuators still suffer from their downside that very large electric fields are necessary for actuation.

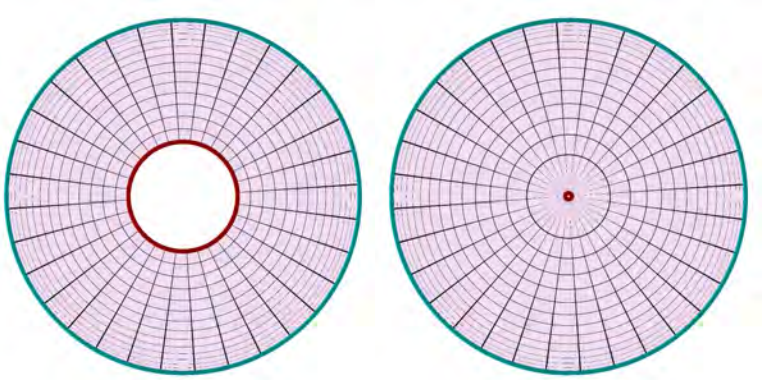

Figure 2: Example of a valve actuator, left: open valve, no voltage applied, right: closed valve upon actuation.

CONCLUSION

Modeling electro-active dielectric and electrostrictive elastomer actuators comprise some difficulties, as not only the large deformations necessitate a geometric nonlinear formulation, but also the material itself along with the inherent electric coupling constitute additional nonlinearities. The presented approach resolves some of the prominent issues and allows to easily incorporate, or drop, any effect relevant for the specific material under investigation. Another strength comes with the computation efficiency, which is of special interest if a control strategy for a collaborative of multiple electro-active elastomer actuators, integrated on a carrier structure, has to be designed. This can be used to trigger a desired motion of the carrier structure, e.g. a wing structure in order to mimic the motion of a bird.

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ELECTRONIC TRANSPORT PROPERTIES AND FERMI SURFACE TOPOLOGY IN CUPRATE SUPERCONDUCTORS.

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INTRODUCTION

The phenomenon of high-transition-temperature (high-T_c) superconductivity is one of the most exciting, thoroughly investigated, yet still unresolved problems in solid-state physics.[1] A major difficulty in understanding high-T_c systems is the complexity of the materials, the presence of strong electron-electron interactions, resulting in rich phase diagrams. The delicate balance among several coexisting phases makes it hard to identify the principal interactions. The copper-oxide superconductors, so called cuprates, in their undoped state are anti-ferromagnetic (AF) Mott insulators,[2] where the charge motion is frozen due to the strong on-site Coulomb interactions. When doped with holes, the anti-ferromagnetic order is quickly suppressed, multiple magnetic and electronic instabilities occur, and high temperature superconductivity (SC) appears.[1,3,4] Beside the origin of the superconductivity, the nature of the pseudogap (PG) regime, associated with opening of partial gaps at the Fermi level, has been an open question for the past three decades. Despite intense studies, the topology of the Fermi surface (FS) within the pseudogap is still strongly debated.[1]

PHASE DIAGRAM OF THE CUPRATES – UNIVERSAL SCATTERING RATE

The superconductivity in the hole-doped cuprates appears above $p \approx 0.05$ (Fig. 1). With increasing the carrier concentration, T_c increases to its maximal value $T_{c,max}$ at $p \approx 0.18$, and then decreases in the overdoped side of the doping-temperature phase diagram.[1] The cuprates in the heavily overdoped regime are quite well understood and can be well described by the conventional Fermi liquid (FL) theory. The resistivity displays quadratic temperature dependence, characteristic of FL.[5] Furthermore, a large, hole-like Fermi surface detected by photoemission and quantum oscillation measurements is consistent with the band structure calculations[6,7] (Fig. 2a). In recent work, it was demonstrated that at moderate doping, in the pseudogap regime, the nature of charge carriers is, in fact, also best described as a Fermi liquid.[8,9] This motivated the attempts to connect the FL properties found in the overdoped regime with those found in the pseudogap (green areas in the phase diagram in Fig. 1). I will present the results of systematic, temperature and doping dependent, electronic transport (resistivity and Hall effect) measurements in single crystals of the model cuprate $HgBa_2CuO_{4+\delta}$ (Hg1201). Results imply that the transport scattering rate $1/\tau$ remains quadratic in temperature upon crossing the pseudogap temperature and entering the strange-metal

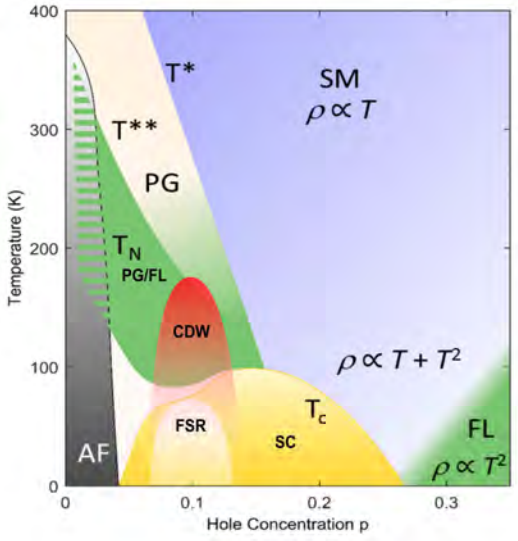

Figure 1: Phase diagram of Hg1201, presenting various phases, discussed in the main text. [10] The red area indicates the charge density wave (CDW) order, which reconstructs the Fermi surface (FSR) at lower temperatures.

phase (SM). Importantly, the comparison of the results with the data available for other cuprate families demonstrates that this key quantity is doping and compound independent, and hence universal.[10–13]

PSEUDOGAP & PERCOLATIVE LOCALISATION OF ONE CARRIER – ARCS

It has long been known that on the overdoped side of the phase diagram, where the FS is large (Fig. 2a), the carrier density corresponds to $n = 1 + p$ (p denotes the doped hole concentration).[6,14] It was also established that the underdoped cuprates have a carrier density that corresponds to $n = p$. Consequently, upon decreasing the hole concentration from the overdoped regime at high doping ($n = 1 + p$) to low carrier concentrations ($n = p$), one hole per CuO_2 unit becomes localized.[13] I will discuss the evolution of the carrier localization occurring upon decreasing doping and temperature. Accordingly, the large hole-like FS, characteristic of the overdoped cuprates, gradually transforms into disconnected Fermi arcs containing p carriers.[13] However, in the underdoped regime, the carrier density increases with temperature, from $n = p$ to $n = 1 + p$, and the Fermi arcs presumably fully close at high temperatures. This gradual (de)localisation gives rise to the exotic strange-metal T-linear behaviour, while the scattering rate remains quadratic in temperature.[10]

SUMMARY & OUTLOOK

Much of the mystery surrounding the strange-metal and pseudogap regimes was demystified by our findings. First, by systematic electronic transport measurements, we demonstrated ubiquitous Fermi-liquid scattering rate throughout the cuprate phase diagram. Furthermore, our work is a major step in the determination of the FS topology of the underdoped cuprates. It suggests that the Fermi surface within the pseudogap consists of Fermi arcs (Fig. 2b), instead of theoretically predicted small hole-pockets (Fig. 2c).[15] This description, of the puzzling features found in the normal state of the cuprates, will presumably allow for a deeper understanding of superconductivity emerging from the normal state.

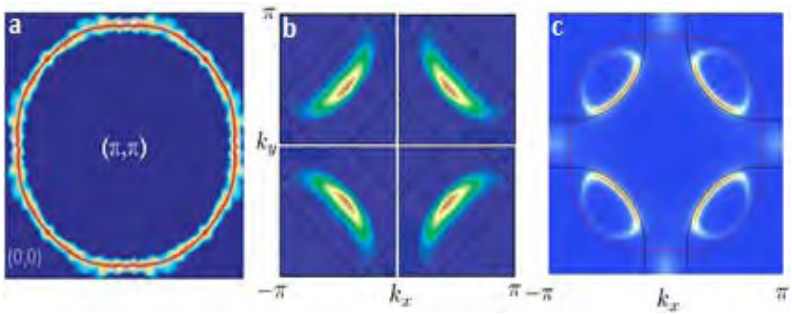

Figure 2. Fermi surface topology of the cuprates. **a** Large FS centred at (π,π) characteristic of the FL regime on the overdoped side. **b** Fermi arcs observed by photoemission spectroscopy within the PG. **c** Fermi pockets theoretically predicted for the PG. **b** and **c** are centred around (0,0).[3, 15]

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STATE OF RESEARCH IN THE FIELD OF DUAL FLUIDIZED BED STEAM GASIFICATION OF BIOMASS WITH IN-SITU CO_2 CAPTURE

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INTRODUCTION

The process of dual fluidized bed steam gasification is a well-known technology for the thermochemical conversion of biomass. Several industrial plants have been built during the last two decades (e.g. in Güssing/AT, Villach/AT, Oberwart/AT, Senden/DE and Gothenborg/SE). The main objectives of these plants are the production of heat and electricity from the produced product gas. Since the increasing prices for wood pellets led to economic troubles of the technology, research activities on the one hand focused on the utilization of cheaper fuels like low grade wood or other residues from agriculture and industrial wastes [1]. On the other hand research focused on further development of the process. Therefore the dual fluidized bed steam gasification with in-situ CO_2 capture (sorption enhanced reforming process or SER) is an innovative evolution, which allows the in-situ adjustment of the product gas composition and therefore is highly suitable for utilization of the product gas as raw material for synthesis processes like methanation or Fischer-Tropsch.

EXPERIMENTS

The SER process uses limestone (mainly $CaCO_3$) as bed material. **Figure 1** shows the basic principle of SER [2], [3]. The combustion reactor supplies heat for the overall endothermic gasification reactions through the circulation of hot bed material particles. Residual char is transported from the gasification reactor to the combustion reactor together with the circulating bed material, where it is burnt to heat up the bed material. Steam is used as a gasification agent and leads to the production of a nitrogen-free and hydrogen-rich product gas. The calcination of the bed material to calcium oxide (CaO) and the release of CO_2 take place ($CaCO_3 \rightarrow CaO + CO_2$) in the combustion reactor at high temperatures. The gasification reactor operates on a lower temperature level. Thus, an in-situ CO_2 capture out of the product gas by carbonation reactions with CaO bed material particles occurs ($CaO + CO_2 \rightarrow CaCO_3$). The decreased CO_2 concentration in the gasification reactor leads to a more intensive water-gas shift reaction ($CO + H_2O \leftrightarrow H_2 + CO_2$) and enhances the production of hydrogen (H_2) in the gasification reactor. Suitable temperature ranges during the SER process depend on the equilibrium partial pressure of CO_2 in the wet product gas and the wet flue gas. **Figure 2** shows a sketch and a picture of the 100 kW_{th} dual fluidized bed gasification pilot plant at TU Wien. All experimental results presented in this work were gained with the pilot plant and validated by mass and energy balances. Therefore all results are highly representative for scale-up of the process.

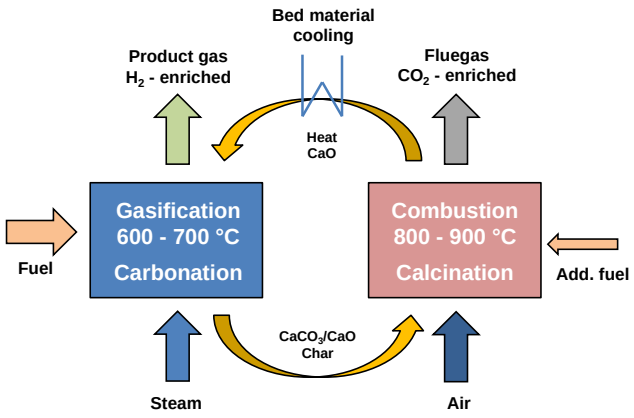

Figure 1: Basic principle of the sorption enhanced reforming process

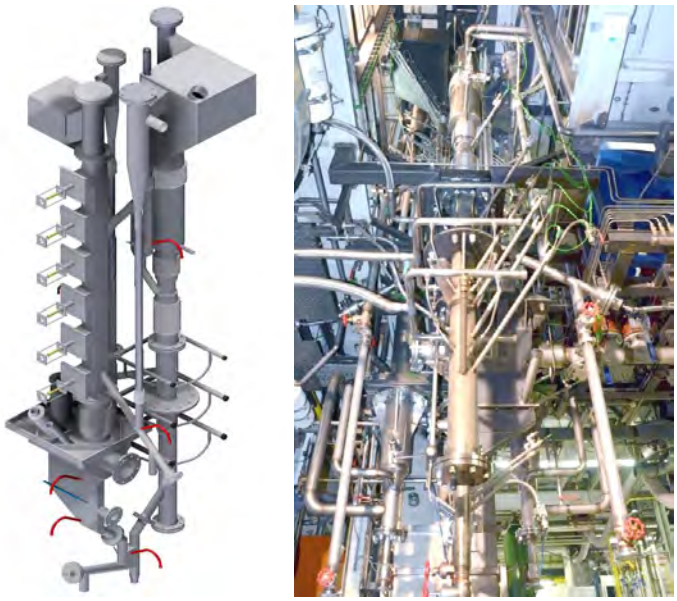

Figure 2: Sketch (left) and picture (right) of the 100 kW_{th} dual fluidized bed gasification pilot plant at TU Wien without insulation

RESULTS AND DISCUSSION

Former research activities mainly focused on the temperature influence of the process. In **Figure 3** (left) it can be seen that for temperatures around 650 °C the lowest CO_2 contents and therefore the highest H_2 contents in the product gas can be observed. However, recent research activities showed that other influencing factors of the process cannot be neglected: The bed material cycle rate is a major factor which influences the product gas composition. **Figure 3** (right) shows that a low cycle rate leads to high H_2 contents in the product gas as well. This points out that also the residence time of the bed material in the reactors is a key factor for the process.

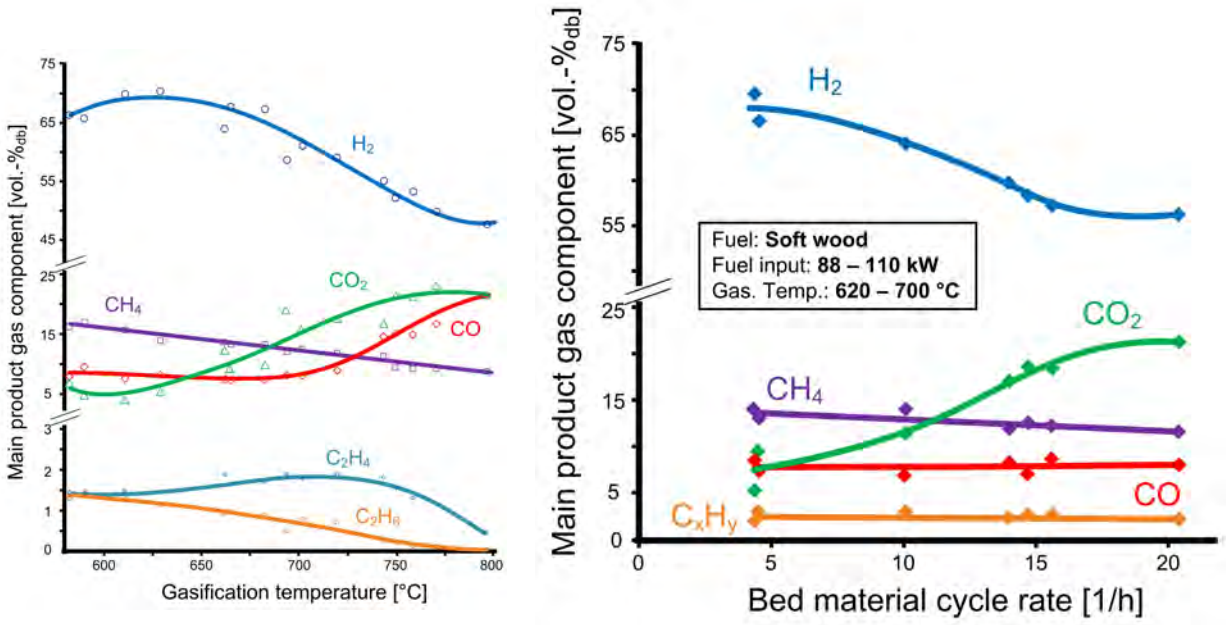

Figure 3: Temperature dependency (left) and bed material cycle rate (right) dependency of the SER process

CONCLUSION

It has been shown that the sorption enhanced reforming process is influenced by different factors. Especially temperature dependency and dependency on bed material cycle rate have been identified. Further investigations will focus on kinetic modelling of the CO_2 sorption of the bed material to identify the limiting factors of the process in more detail.

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SELECTIVE ETHANOL OXIDATION ON SUPPORTED BIMETALLIC GOLD CATALYSTS: BASE CHEMICALS FROM "GREEN" PROCESSES

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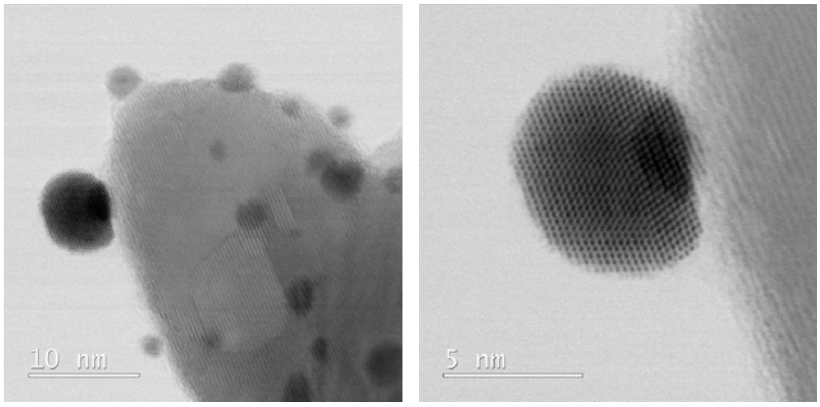
INTRODUCTION

Both acetaldehyde and acetic acid are important base chemicals produced on large scale. Thus, a "green" heterogeneous process accessing renewable feedstocks such as (bio-)ethanol is highly desirable. Bimetallic catalysts have gained much interest as they offer a wide range of possibilities to tune catalytic properties by the choice of the second metal component. We study the selective oxidation of ethanol to acetaldehyde or acetic acid using highly performant bimetallic gold catalysts supported on titania with Ag and Ru as promoters, both of which have a high affinity towards O_2[1-3] (relevant for the activation of molecular oxygen as "mild" reactant).

EXPERIMENTS / FUNDAMENTAL OF THE PROBLEM / EXAMINATIONS

Catalysts are prepared with Deposition Precipitation (Au catalysts) and Incipient Wetness Impregnation (AuAg prepared from the Au catalysts): 5 wt.% Au and 1 wt.% Ag/Ru on titania. Rutile, Anatase and (commercial) mixtures of Rutile and Anatase were evaluated as support materials. The samples underwent thorough evaluation of their catalytic properties in gas-phase as well as in (aqueous) liquid phase (at the ETH Zurich[4]). In gas-phase, the influence of H_2O (on the reaction rate as well as the product distribution) was investigated.

However, the mechanism of oxygen activation (and the role of the catalyst support in it) as well as the structure of the of the bimetallic metal particles (segregation effects, alloy formation, surface oxides, eg. AgO_x) are still poorly understood. Catalyst materials were characterized by HR-(S)TEM (see Picture 1), STEM-EDX as well as XRD and XPS (to determine the surface composition and the oxidation states of the metal nanoparticles and the Ti(III)/Ti(IV) ratio). Moreover, operando studies were performed: DR-UV-Vis spectroscopy was used to monitor the evolution plasmon bands of the bimetallic nanoparticles and reactive species on the catalyst surface were monitored using DRIFTS, thus giving insight into the reaction mechanism. Experiments were backed by DFT calculations from our project partners at the Ghent University.



Picture 1: HR-STEM micrographs of the AuAg nanoparticles on TiO_2.

RESULTS AND DISCUSSION

Both Ag and Ru show a strong synergistic effect with Au: AuAg and AuRu show high-conversion and long-term stability of at least 72 hours in combination with a high resistance against sintering. In gas-phase, selectivity is throughout > 95% with acetaldehyde as the main product and mainly methyl-acetate and acetic acid as side products. In contrast to that, in (aqueous) liquid phase acetic acid is the dominant product (and pure Au or AuPt is more beneficial than AuAg or AuRu). Even with an EtOH/H_2O ratio of 1:2, this shift from acetaldehyde to acetic acid cannot be achieved in gas-phase.

Rutile is by far the best catalyst support, outperforming both Anatase and mixtures of Anatase/Rutile (probably also because of the less beneficial distribution of the metal nanoparticles between Anatase/Rutile as reported in[5]). Differences in oxygen vacancies/mobility between Rutile and Anatase are suspected are to be confirmed by operando XPS studies.

Preliminary XAS as well as (ex-situ) HR-STEM-EDX measurements show evidence for alloy formation. Operando DRIFTS measurements revealed a relatively clean surface of the catalyst, which is in alignment with DFT calculations (clean surface for Au(111) and an alkoxy-covered surface for Ag(111)). The exact role of (possible) Ag/Ru surface segregation (and its possible influence on sintering as reported for AuIr systems[6]) and alloy formation under dynamic conditions will be studies in future operando XAS and XPS beamtimes in the first half of 2018.

CONCLUSION

AuAg as well as AuRu have proven to be performant catalysts for the oxidation of ethanol to acetaldehyde with high selectivies (> 95%) and excellent long-term stability. In gas-phase, the main product is acetaldehyde, whereas in aqueous solution in liquid phase acetic acid is formed.

Alloy formation was observed for AuAg and evidence for the oxidation of Ag and Ru was found. For AuRu, we show irreversible storage damage due to Ru(IV) formation.

Operando XAS and (near ambient pressure) XPS (first preliminary results to be presented at the VSS) will shed light on the electronic structure, possible (surface) segregation of Ag/Ru, and alloy formation of the catalyst under dynamic reaction conditions.

Thus, bimetallic Au supported on titania is a promising catalyst for a green heterogeneous ethanol oxidation under mild conditions (best operating conditions at approx. 250°C) with molecular oxygen as oxidant.

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CRYSTALLOGRAPHY AS A VERSATILE RESEARCH TOOL

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INTRODUCTION

In order to exemplify methods of contemporary crystallography, two cases are discussed in the present contribution: the results of a research publication of the redetermination of a crystal structure and the results of ongoing investigations of catalytically active, amorphous networks. This contribution is intended to give insights into the physical theory applied as well as refinement strategies on a basic level.

ALLOTWINNIG IN THE MIXED CARBONATE $KAgCO_3$

In the first example, the redetermination of the crystal structure of $KAgCO_3$ is discussed [1]. It is based on crystals made up of two different polytypes with *Pccb* and *Ibca* symmetry, respectively. Motivation was given because in one of the reported structural characterizations of $KAgCO_3$, violations of the systematic absences of the *Ibca* space group were noted.

Crystals of $KAgCO_3$ belong to an order-disorder (OD) family of structures composed of layers of two kinds. Sharp diffraction spots and the absence of diffuse scattering indicate highly ordered macroscopic domains. There are two polytypes with a maximum degree of order [MDO_1: *Pccb*; MDO_2: Ibca, doubled a-axis compared with MDO_1], which are both realised to a different extent in two crystals under investigation. In the case at hand, different structures can be generated by stacking differently orientated layers. An allotwin model (addition of the intensities of both domains) was used for simultaneous refinement of the structure of $KAgCO_3$ against all reflections.

Figure 1 shows a sub-division of the structure into different layers and the unit cell doubling in the second polytype.

DETECTION OF NANO-PRECIPITATES IN AN AMORPHOUS MATRIX

The second example is delicate. Investigation of a material with alleged catalytic properties ([3]) by pair-distribution-function (PDF) analysis ([2]) was performed. Rutile (TiO_2) nano-particles could be modeled together with an amorphous-matrix (a-SiO_2)

Strictly speaking, it is forbidden to apply established practices for data treatment in the PDF-methodology here, as the material is constituted by multiple phases. It is an interesting finding that it was possible however, to satisfactorily describe the measured PDFs by means of the PDFs of crystalline rutile, fused quartz and a modulation wave. While this might be an indication for a restructuring of the amorphous matrix around the particles as is known from colloid studies, further methodological research must be performed to elucidate the reliability of the results. The refinements are shown in figure 2.

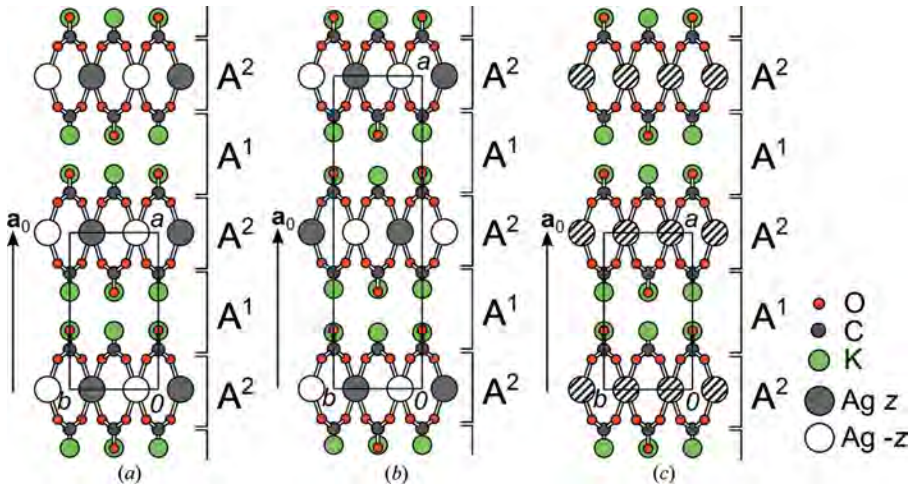

Figure 1: The (a) MDO_1 (*Pccb*) and (b) MDO_2 (*Ibca*) polytypes, and (c) the family structure of $KAgCO_3$ viewed down [001]. Ag atoms at (x, y, z) and (x, y, -z) by large grey and white spheres or, if both positions are occupied, by hatched spheres. Other color codes are given in the legend. Layer types are indicated to the right.

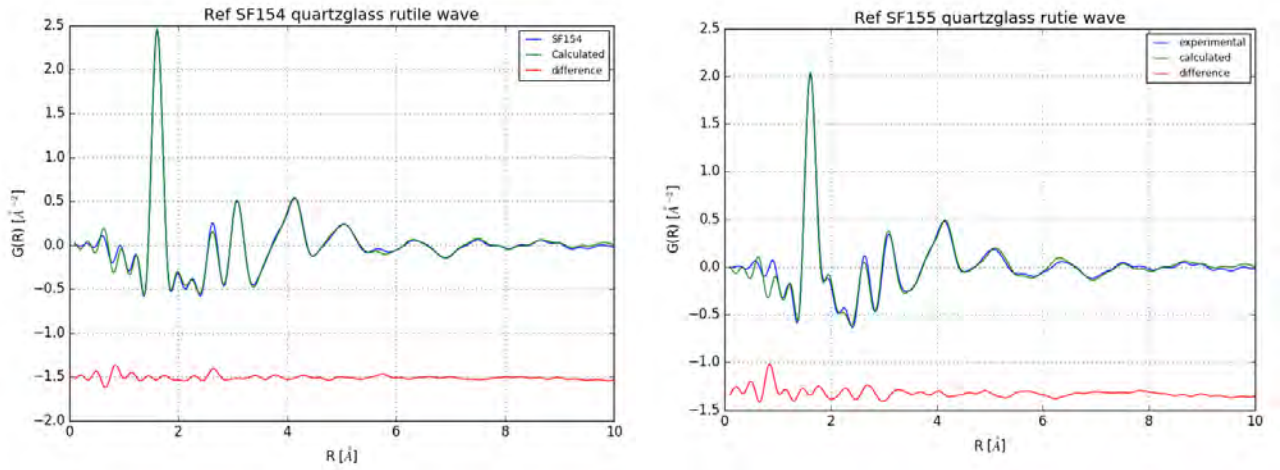

Figure 2: For two similar materials, rutile-particles with extensions of only a few unit cells, could be incorporated into a model that satisfactorily described the measured PDFs G(r). This is interesting as in the theoretical framework, a considerable error is expected for polyphasic materials.

CONCLUSION

Properly applied, the tools of crystallography exhibit great capabilities to structural solution complex materials. In this contribution, research results are to be discussed and analysed in terms of their trustworthiness.

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$Au_n(SR)_m$ NANOCLUSTERS: TOWARD ATOMICALLY DESIGN NANOCATALYSTS

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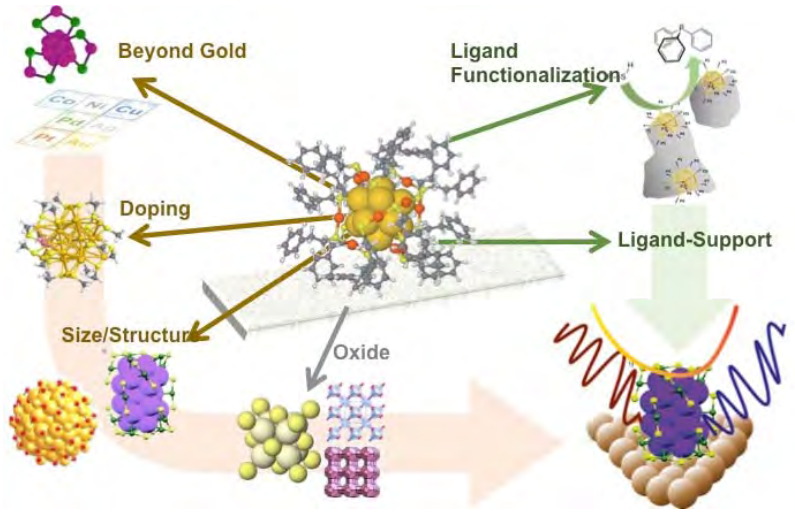
INTRODUCTION

Nanoscience has recently revolutionized catalysis R&D, both at academic and industrial levels. To understand and control the catalytic performance of nanoparticles at molecular level is a major challenge and ultimately to bridge the gap between model and real catalysis. Metal clusters are well-defined nano-size systems that contain a precise number of atoms (few to 100) with specific elemental composition (e.g. Au, Ag, Pd,…). Advanced synthesis routed yield nanoclusters with high purity and homogeneity, with well-resolved and unique crystal structure. Their catalytic properties are often unexpected and remarkable, and differ strongly from those predicted by simple scaling laws, due to their quantized electronic and unique geometrical structure. Thiolate protected metal nanoclusters ($M_n(SR)_m$) open up new possibilities to create atomic precise catalytic active sites with resolved structures. A truly monodisperse catalytic surface provides ideal conditions for structure reactivity correlation studies. In our studies, we explore the design of catalytic active sites at atomic level with the monolayer protected metal clusters. Different metal combinations have been explored such as PdAu or PtAu.[1] The interaction with different oxides supports and their properties evolution under different treatments have been studied by several techniques (FTIR, XAFS, XPS, HRTEM…).[2] The final application for catalytic oxidation and photocatalytic reactions, in gas and liquid phase have been explored and analysed in in situ operando techniques in order to correlate their catalytic properties with the structure and properties of the cluster catalysts.[3,4]



Picture 1: Scheme of cluster tuning properties possibilities for catalytic

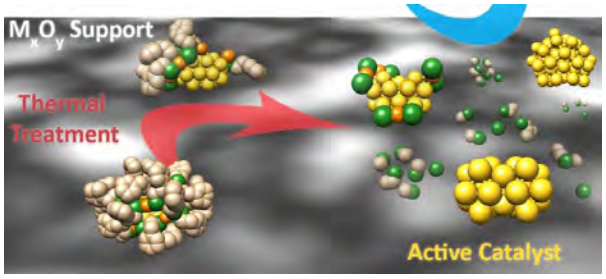
EXPERIMENTAL

Monometallic and bimetallic thiolated metal clusters have been synthesized by optimized protocols based on Brust method.[1-4] Their purification and isolation were obtained by SEC (size exclusion chromatography) and HPLC, and analysed by MALDI and UV-Vis. The physical-chemical properties, their structure and their reactivity, were investigated by X-ray Absorption Spectroscopy (XAFS) at several synchrotron sources (SLS, ALBA…), XPS, STEM, STM between others.

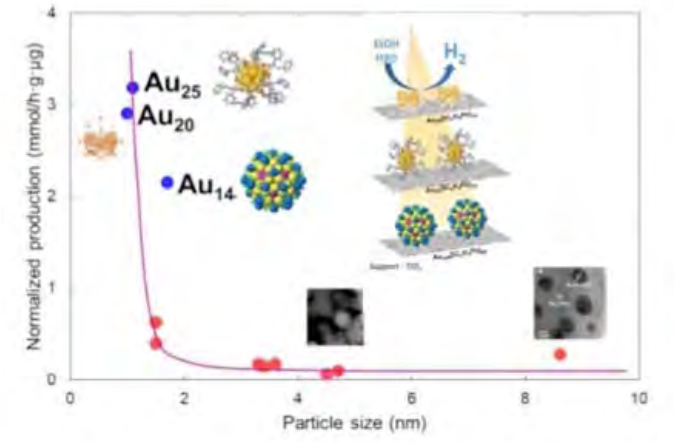
RESULTS AND DISCUSSION

The clusters significantly promote molecule activation by enhancing the adsorption energies of the reactant molecules on the catalyst surface. However, the stability under pretreatment and reaction conditions is strongly related with the nature of the support material. Several oxides have been

studied as support material for the Au clusters, among them, cerium oxide (CeO_2) turned out to be one of the best in our previous studies. The thiolate ligands around the gold core structure play an important role in the cluster stabilization and their catalytic activity. Once the clusters are supported, the ligands can be thermally removed in order to expose a larger gold surface area to the reactants. Depending on the degree of ligand removal, different catalytic activity and selectivity can be obtained for several oxidation reactions, due to changes in electronic configuration or available sites. In our previous studies, *in situ* EXAFS measurements indicated that the degree of thiolate ligand removal depend on the heating atmosphere and the support material. S K-edge measurements performed of fresh and used (after cyclohexane oxidation reaction) catalysts pre-treated at different temperatures were studied ex-situ. The results pointed out the different interaction of the thiol ligands depending of the support material after thermal treatment and also after reaction, observed for first time. XANES results at S K-edge show sulphur species at different oxidation states at the different stages. This could be related with the changes in catalytic/selectivity performance of the cluster catalysts in the different oxidation reactions. In the last study we focused on the structure stability of Au_{38}/CeO_2 under CO oxidation by operando Au L_3 edge XAFS. The results denoted the high stability of the Au_{38} cluster structure during the reaction and the requirement of the pre-treatment in order to obtain such stability. In our latest studies, Au_n clusters supported on TiO_2 have been studied in photocalytic reactions. The comparison with the pair gold nanoparticles shows the clear enhancement of the gold nanoclusters in the photocatalytic performance.



Picture 2: Graphical Scheme of Cluster Catalysts surface evolution under treatment and reaction



Picture 3: Photocatalytic activity depends on size and structure

CONCLUSION

Monolayer protected clusters have shown their outstanding performance in several catalytic reactions, allowing an unique homogenous and defined surface. Their stability under reaction conditions and their possibility of atomically level design will open a broad number of studies for not only catalytic applications.

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ENHANCING CATALYTIC ACTIVITY BY ELECTROCHEMICALLY DRIVEN METAL NANOPARTICLE EXSOLUTION

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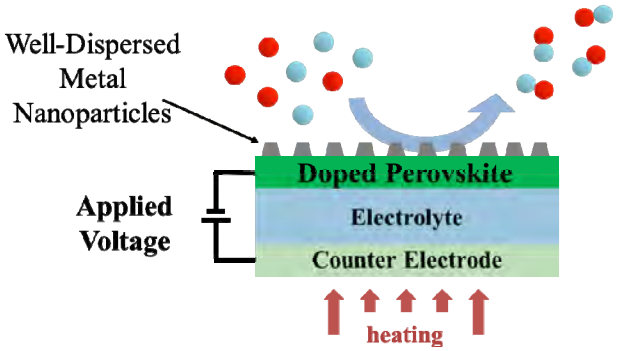
INTRODUCTION

In heterogeneous catalysis surfaces decorated with uniformly dispersed, catalytically highly active particles are a key requirement for excellent performance. One of the main tasks in catalysis research is the continuous improvement or development of catalytically active materials.

An emerging concept in catalyst design is to selectively and reversibly tune and modify the surface chemistry by electrochemical polarisation. Perovskite-type catalysts raise the opportunity to incorporate guest elements as dopants. Upon electrochemical polarisation these dopants emerge from the oxide lattice to form catalytically active clusters or nanoparticles on the surface (by exsolution). In consequence this leads to a strong modification or enhancement of catalytic selectivity and activity. Electrochemical polarisation offers the possibility to adjust the surface chemistry in response to an external signal in real time (here by the applied voltage).



Picture 1: Setup for operando measurements with electrochemical polarization of the surface. Polarization leads to the formation of the metal nanoparticles, which are then enhancing the catalytic activity.

EXPERIMENTS

We present studies for high temperature water splitting[1] and CO_2 electrolysis[2] in a realistic catalytic reaction environment (operando), on different acceptor doped perovskite-type electrodes, and show a direct correlation of surface chemistry with catalytic activity, selectivity and the electrochemical stimulation. This is achieved by a unique combination of surface science, heterogeneous catalysis and electrochemistry.

The experiments were performed at the ISISS beamline of the HZB/BESSY II synchrotron in Berlin with the near-ambient pressure high energy XPS setup (NAPHE-XPS). In this setup XPS and XAS measurements can be performed at elevated pressures (up to 7 mbar) and X-ray energies from 80 to 2000 eV. The setup consists of a high pressure cell with an attached differentially pumped hemispherical analyzer (modified SPECS Phoibos 150) including a 2D delay line detector. For a detailed description of the setup see reference[3].

RESULTS AND DISCUSSION

Exsolution of metallic particles from the perovskite lattice does not affect the kinetics of CO_2 splitting, which is a distinct difference to high temperature H_2O electrolysis were the kinetics were strongly improved. This also contradicts conclusions made from electrochemical CO_2 splitting

measurements with porous perovskite electrodes and supports the importance of the use of model-type electrodes.

The perovskite electrode materials exhibit a rather high coking resilience with carbon deposition only occurring under strongly cathodic polarization. Moreover, the detrimental effects of carbon were completely reversible upon retracting the applied bias without damaging the electrode, which is a very promising result from an application point of view.

FUNDING

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SUPPORTED GOLD NANOCLUSTERS: EFFECT OF CLUSTER SIZE AND OXIDE MATERIAL UNDER OXIDATION PROCESSES

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INTRODUCTION

Heterogeneous catalysis by metal nanoparticles supported on oxides is often limited in activity/selectivity, due to variations in metal particle size, surface structure and bonding to the support. Thiolate-protected Au nanoclusters have shown enhanced catalytic activity in several processes in comparison with the common nanoparticle catalysts. Atomically designed metal clusters offer the possibility to design well-defined and truly homogeneous surfaces, leading to optimal catalysts for reaction mechanism studies. However, understanding the stability of the cluster structure and type of interaction with the support during the thiolate ligand removal treatments and under reaction conditions represent key understanding for their catalytic application [1].

EXPERIMENTS

The interaction and stability of $Au_{25}(SC_2H_4Ph)_{18}$ and $Au_{144}(SC_2H_4Ph)_{60}$ clusters on different oxide materials (SiO_2, TiO_2 and ZrO_2) have been studied by (UV-Vis, TGA, FTIR, HRTEM, XRD and XAFS). Supported clusters were pretreated under air (a common industrial pretreatment) at 150°C for a partial removal of ligands and at 250°C for a total removal of ligands. In order to establish correlations between morphology and catalytic properties, cyclohexane oxidation was employed as a model reaction, as it is a well-known industrial process where gold is required to activate the molecular oxygen.

RESULTS AND DISCUSSION

TGA studies showed that the removal of ligands takes place around 200°C. In order to find out more about cluster´s stability under harsh conditions, particle size images were measured after loading and after both pretreatments. HRTEM images showed that there is a negligible increase of particle size after 150°C, while a significant increase was observed after 250°C.This size increase was also noticeable via diffuse reflectance spectroscopy. The spectra changes considerably after 250°C pretreatment, a new band is observed at 520 nm corresponding to the surface plasmon resonance band, characteristic of particles bigger than 2 nm and reflects the collective excitation behaviour in metallic state. Measurements of pretreated and unpretreated samples were also performance using synchrotron radiation. We observed a higher structural stability of $Au_{144}(SC_2H_4Ph)_{60}$ compared to $Au_{25}(SC_2H_4Ph)_{18}$.

Moreover, we compared the catalytic activity and selectivity of both clusters supported on SiO_2, TiO_2 and ZrO_2 as well as the pretreatment influence in the catalytic activity. Cluster´s stability after reaction was also probed with XRD, the results confirm that the structure is preserved after 10 hours reaction, making this clusters recyclable.

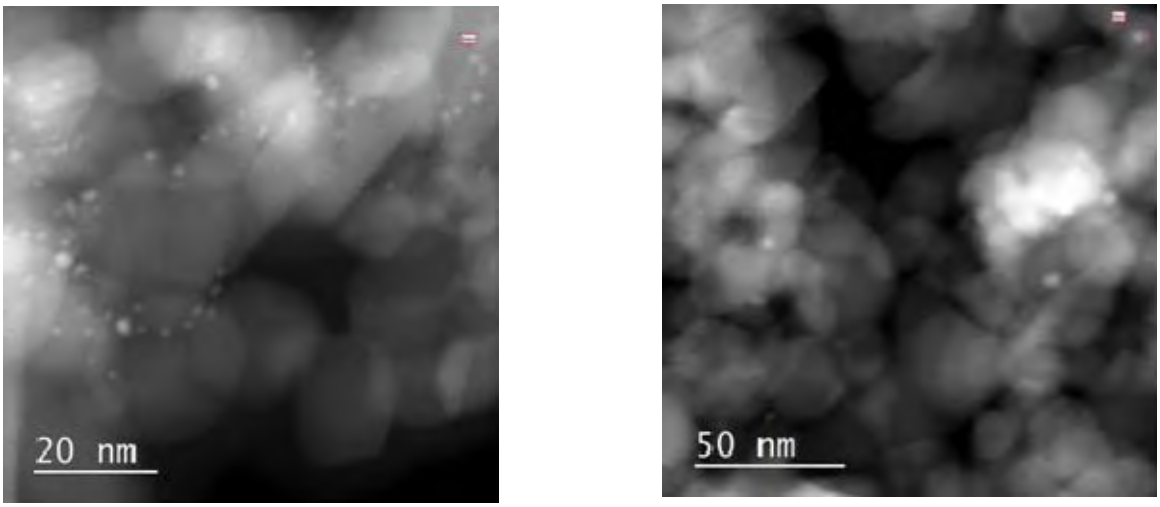

Figure 1: HRTEM images of 2% wt $Au_{144}(SC_2H_4Ph)_{60}/TiO_2$ after 150°C pretreatment (left) and after 250°C (right)

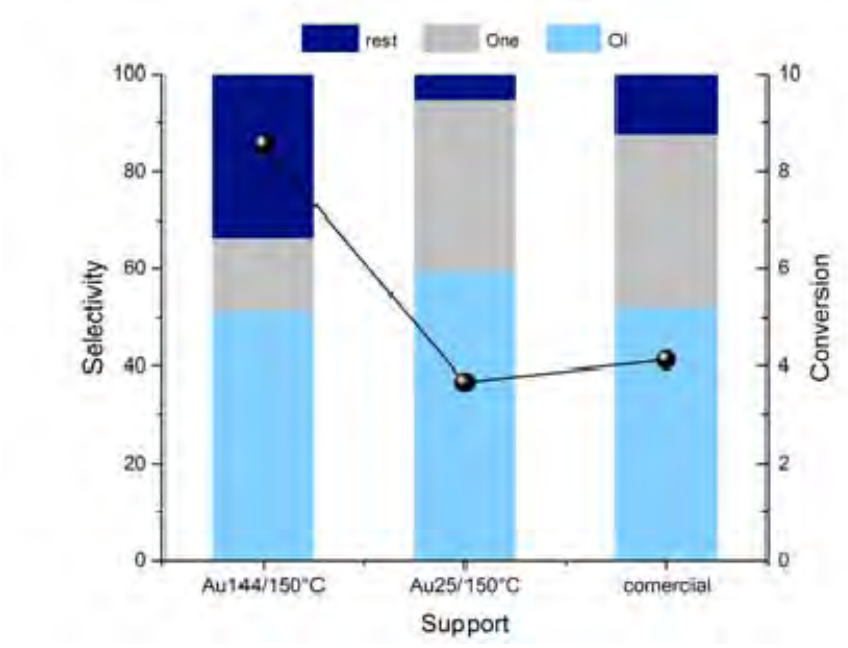

Figure 2: Conversion and selectivity in cyclohexane oxidation after 10h.
The main products are cyclohexanol (ol) and cyclohexanone (one).
Peroxide was used as a iniciator.

CONCLUSION

It was observed that a 150° leads to a partial removal of ligands, activating the catalyst as well as preserving the particle size. $Au_{144}(SC_2H_4Ph)_{60}$ supported in TiO_2 lead to the best values of selectivity and conversion, compared with traditional commercial nanoparticles and with smaller clusters. This high activity may be associated with the unique geometric structure (icosahedron). We can also conclude that TiO_2 not only stabilizes the cluster, but also plays an active role in the reaction. The results here opens doors for further application of thiolate gold clusters in liquid phase reactions.

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MATERIAL DESIGN FOR PHOTOCATALYTIC H_2 PRODUCTION FROM WATER SPLITTING

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INTRODUCTION

Energy has been defined as the top of the ten challenges that our society faces and exploitation of renewable energy has become a vital task. Hydrogen has attracted researchers' attention as a green alternative fuel. There are two green ways for hydrogen production, electrocatalytic and photocatalytic water splitting. Compared with electrocatalytic water splitting, photocatalytic water splitting (PCWS) bears the advantages of using abundant solar light instead of electricity and therefore, can be considered as a way more sustainable technology. The working principles of PCWS can be summarized by Fig.1. Under light illumination, semiconducting catalysts generate photo excited electrons and holes. These excitons can separate and become free-moving charges. Then, the charges can transport to the surface of the catalyst and transfer to the adsorbed species to form H_2 and O_2. For the moment, PCWS still suffers from rather low overall efficiency as a result of insufficient charge separation, charge transportation to the interfaces, or charge transfer from the interfaces to the reactant medium that all contribute to the final quantum yield values. Besides, catalyst deactivation[1] can also happen and result in strong sudden drops of the energy conversion efficiency during the photocatalytic process.

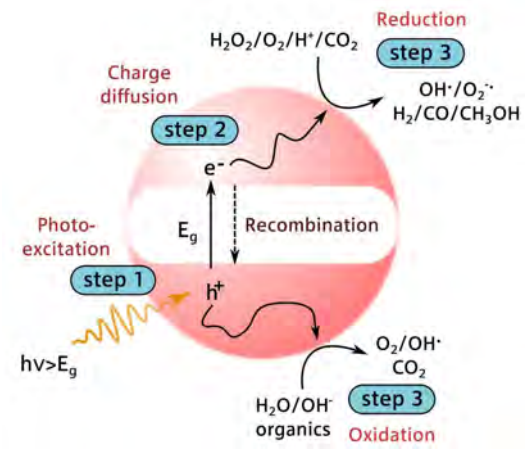

Figure 1. Schematic illustration of working principles of photocatalytic water splitting

FUNDAMENTAL OF THE PROBLEM

To improve the efficiency of photo-driven water splitting, to face those above-mentioned challenges, we follow several strategies. (a) To harvest more photo-generated charges, catalysts with more suitable bandgaps have been investigated. The value of the band gap defines the threshold energy of absorbed photons, while its position has a strong impact on electron and hole injection over-potentials. (b) Hybridization[2] of photocatalysts with various materials (e.g. nanocarbons and other metal oxides) has been proven promising to facilitate the charge separation process and reduce charge recombination due to the formation of p-n junctions or quick extraction of one of the charges by the second component. (c) Meanwhile, nano structuring of photocatalysts is favourable for efficient charge extraction from bulk to the surface where the ultimate catalytic reaction takes place. Moreover, mesoporous catalysts with accessible pores provide more reactive sites between catalysts and reactants[3].

Figure 2. Reactor for water splitting

RESULTS AND DISCUSSION

Based on the above discussions, we have rationally designed a number of materials for efficient H_2 generation. As shown in Fig.3, hybrid Ta_2O_5/CNT (Fig.3a) was prepared that performed superior compared with pure Ta_2O_5. The presence of carbon nanotube (CNT) indeed facilitated charge separation and reduced charge recombination leading to more charges available for the catalytic conversion. By using the self-assembly of triblock-terpolymer PI-PS-PEO, 3D mesoporous structure of Nb_2O_5 with suitable 10-30 nm pore sizes and long-range order were prepared (Fig.3d). Our photocatalytic H_2 evolution experiments demonstrate that nanostructured photocatalysts with high and accessible surface and short migration lengths for photoexcited charge carriers are primary candidates for high-performance photocatalysts. Therfore, mesoporous Ti-based metal-organic framework (MIL 125-MOF) and its metal oxides (Fig. 3c) were also investigated for PCWS. Furthermore, defects were found to trigger early-stage deactivation in the traditional photo-catalyst TiO2 with photodeposited Pt as co-catalyst (Fig.3b). Key to this phenomenon is the ratio of Pt atoms to oxygen vacancies, which were created through ultrasonic pretreatment and in situ UV irradiation in the bulk and surface, respectively. Additionally, a possible surface passivation of Pt was observed that could be analogue to known strong metal-support interactions of reducible metal oxides. Pre-calcining the photocatalyst resulted in a stable rate during the course of the experiment.

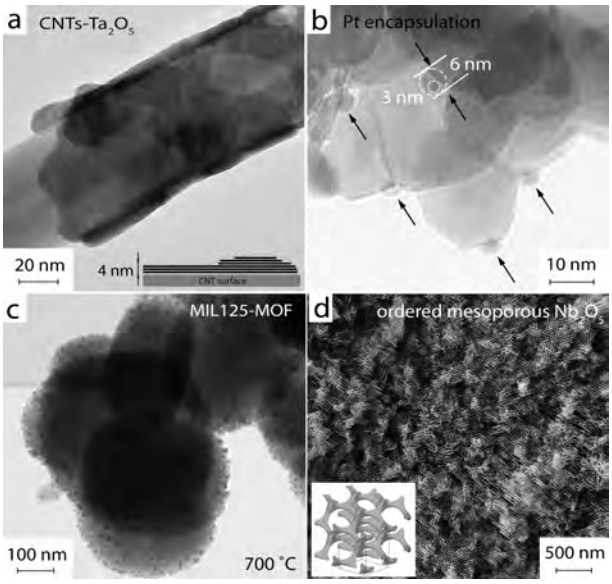

Figure 3. TEM images of novel catalysts designed for more efficient water splitting

CONCLUSION

Actually, these strategies inter-played with each other and are complimentary to each other. Rational material design based on these strategies contributed to minimize the challenges and to improve water splitting efficiency.

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ENVIRONMENTALLY FRIENDLY GENERATION OF HIGH-PERFORMANCE POLYIMIDE FOAMS USING MONOMER SALTS

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INTRODUCTION

Polyimides (PIs) are polymers whose backbones comprise mostly aromatic and heteroaromatic moieties connected by typically cyclic imide functions. They are materials of the utmost thermal, chemical and mechanical stability [1], and hence they are applied in high-performance sectors such as aeronautics and microelectronics. Unfortunately, the superior materials properties of PIs come at the high cost of being conventionally synthesized under harsh and demanding conditions [2]. In classical syntheses (Figure 1 A) the comonomers diamine and dianhydride are employed and first reacted to poly(amic acid) intermediates, which are subsequently converted to the final PI by thermally induced condensation cyclizations (typically referred to as “baking” or “curing”). These classical syntheses use high-boiling and toxic solvents such as dimethylformamide (DMF), and toxic catalysts such as isoquinoline. Furthermore, long reaction times (t > 8 h) at elevated temperatures (T up to 450 ˚C) are necessary.

FUNDAMENTAL OF THE PROBLEM

Alternatively, one can prepare a salt-type single-source precursor, which contains both necessary comonomers of PIs. These so-called monomer salts, *i.e.* ammonium carboxylate salts (Figure 1 B) are highly advantageous as starting materials. First, they intrinsically provide ideal stoichiometry of the comonomers, which is of the utmost importance in order to obtain high-molecular weight polymers according to Carothers’ law. Second, the fact that the comonomers are bound in the form of a salt increases storability. In contrast, the pristine diamine comonomers require storage with special precautions such as the absence of oxygen.

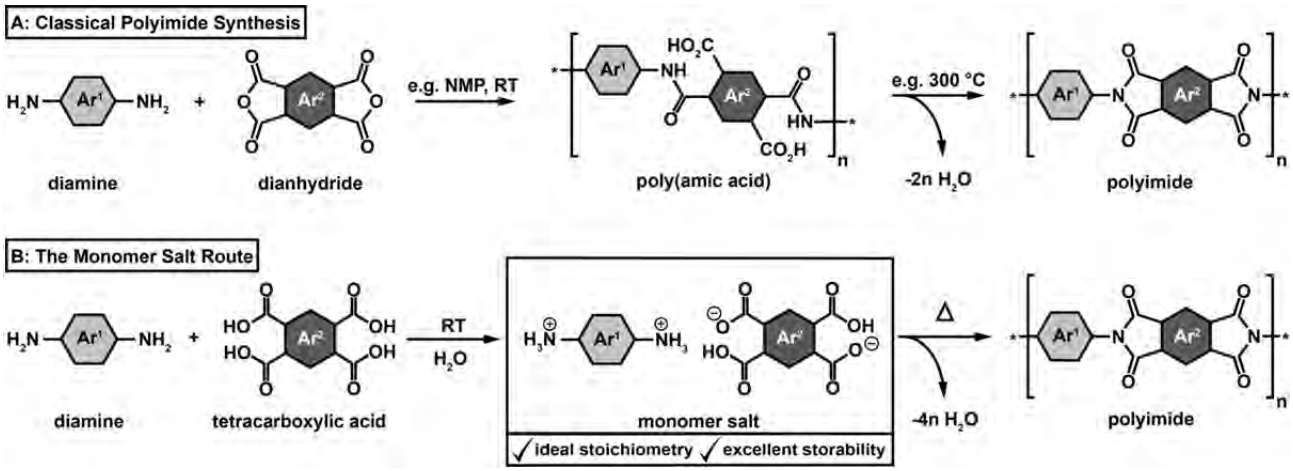

Figure 1: A – Classical two-step procedure towards PIs from an aromatic dianhydride and an aromatic diamine *via* a poly(amic acid) intermediate. B – The monomer salt route in which a single-source salt precursor is first generated by acid-base reaction, and subsequently thermally imidized.

The preparation of monomer salts is straightforward: They are simply obtained by an acid-base reaction between the comonomers (Figure 1 B, first step) and can be transformed to PIs by

subsequent heat treatment (Figure 1 B, second step). This transformation process is called solid-state polycondensation (SSP). As SSP is a solvent-free route, it can be classified as a "green" method and is therefore of great scientific, ecological and economic interest. Polyimides from SSP often show intriguing properties that are a direct consequence of the polymerization process, such as increased porosity [3], and conservation of the initial monomer salt's shape [4].

RESULTS AND DISCUSSION

We discovered a novel monomer salt as precursor for polyimides that upon heating does not conserve its initial shape, but instead goes through a liquid-like state prior to polymerization. Such softening has only rarely been observed in PI syntheses employing the monomer salt route: these syntheses typically take place in the solid-state. This liquefaction enables the formation of a continuous PI phase, which appears to have a foam-like form. The foaming behavior is partially due to the water vapor arising from the polycondensation reaction (*cf.* Fig. 1). Additionally, the foaming process is promoted by a peculiar and to date unreported demixing of the condensation byproduct water from short-chain oligomers forming at the beginning of the thermally induced polymerization. We herewith present this unique monomer salt, including its crystal structure as determined from single crystal X-ray diffraction (SC-XRD). Furthermore, the system was characterized using powder X-Ray diffraction (PXRD), scanning electron microscopy (SEM), infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The fact that this monomer salt allows for generating high-performance polyimide foams without the need for any organic solvents or foaming agents makes the route intrinsically green. Moreover, the novel monomer salt is easily synthesizable and easily storable under ambient conditions and all that at a very low cost of all involved compounds.

CONCLUSION

With this contribution, we present a novel monomer salt as precursor for polyimides, which is perfectly suitable for producing high-performance polymer foams. The novel monomer salt shows unusual behavior upon thermally induced polymerization. Most importantly, the peculiar combination of the monomer salt's softening with phase separation of freshly formed oligomers from the condensation byproduct allows for generating PI foams without the need to add foaming agents or organic solvents. Hence, the presented monomer salt lays the basis for the environmentally friendly generation high-performance polyimide foams.

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DRY TRANSFER PROCESS OF MO_X NANOWIRES USED FOR GAS SENSING APPLICATIONS

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INTRODUCTION

Monitoring of environmental conditions via gas sensing devices is currently of high interest for air pollution control. One of the most important material systems applied to gas sensors are metal oxides due to their high sensitivity – especially in the form of nanomaterials such as nanowires (NWs) and nanoparticles. Those structures demand proper implementation in gas sensor devices. In this paper we report dry transfer technology of SnO_2 NWs to gas sensor substrates and their gas sensing performance. Silicon-based sensors with gold inter-digital electrode structures (IDES) were produced and high sensitivity to H_2S gas was demonstrated. Simple transfer process with polydimethylsiloxane (PDMS) stamp was employed and potential applications in the future were shown.

EXPERIMENTS

SnO_2 nanowires were synthesized by two-step synthesis[1]. First a SnO_2 thin layer (400 nm) was deposited on a Si-substrate by spray pyrolysis technique. Then the SnO_2-sample was placed in a tube furnace with another Si-substrate coated with a thin catalytic metal layer (i.e. 40 nm copper). The samples were mounted parallel to each other with the SnO_2-coated Si-substrate on the bottom and the Cu-coated Si-sample on top with a spacing of 1 mm in between so that the layers were facing each other (“face to face”), The subsequent annealing process was performed for 3 hours in Ar-atmosphere at a temperature of 900°C and resulted in SnO_2 NW growth on the metal-coated Si-sample. Average diameters and lengths of the SnO_2 NWs were 50-200 nm and 10-100 µm, respectively.

The transfer process of SnO_2 NWs was performed as follows: first a specific PDMS stamp was prepared. Dow Corning Sylgard 184 base and curing agent were mixed in a 10:1 ratio by weight and annealed at 100°C in flat Petri dish (stamp – 5x5 mm piece was used). Next the MOx NWs were picked up manually by the stamp and were transfer printed on Si-based gas sensors with Au-IDES as electric contacts (Fig. 1). The print transferred SnO_2 NWs electrically connect the electrodes and serve as gas sensing elements. As a result resistance measurements can be performed along the NWs in the presence of various target gases. The gas sensor with MOx NWs on top was glued on micro heaters (10×2 Pt 6.8 Delta-R GmbH) and thermocouple (4×1 Pt100, Delta-R GmbH) and bonded on chip carrier (mb-Technologies GmbH).

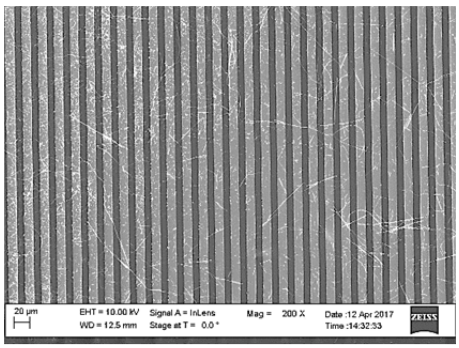

Figure 1: SnO2 NWs on Au-IDES gas sensor substrate.

RESULTS AND DISCUSSION

Gas measurements were performed in an automated gas measurement setup. The flow rate was kept constant at 1000 sccm and synthetic air (80% N_2, 20% O_2) was used as background gas. The resistance of the NW sensor devices was measured in constant current mode (10nA) and in different hydrogen sulfide concentrations ranging from 10 to 1000 ppb. The gas response was investigated at constant temperature – 400°C and three different relative humidity (rH) levels: 25%, 50%, and 75%. The sensitivity for each gas concentration and humidity level was calculated as follows:

$$S = \frac{R_{air} - R_{gas}}{R_{air}}$$

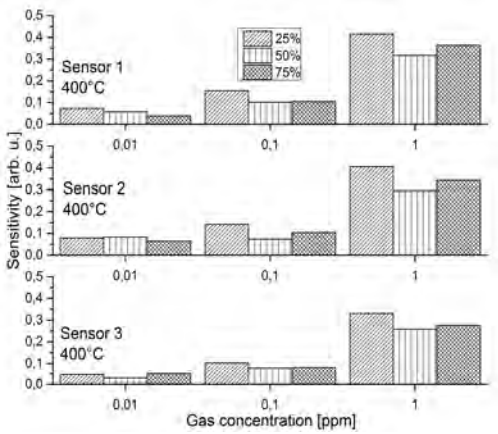

Figure 2: SnO_2 NWs gas sensor sensitivities for three different sensors produced by the same transfer method.

The measured sensitivity performance of three different sensors (produced the same way) are shown in Fig.2: the results are comparable which demonstrates a good reproducibility of sensor fabrication although the transfer process is performed manually. Highest sensitivity for each of the sensors was achieved at lowest humidity level, which shows that the sensors have also cross-sensitivity to humidity.

The integration of MOx NWs on gas sensor substrates with dry transfer print process demonstrates that this comparatively simple and low cost technology can be employed to fabricate nanomaterial-based devices. Previously we have integrated MOx NWs on CMOS-based micro-hotplate arrays using drop coating and ink-jetting techniques[2]. For these technologies solvents have to be employed that might have detrimental properties on the gas sensing properties because of organic residuals. The advantage of the print transfer method is that it is a dry non-solvent based technique. However, both technologies are presently used for the development of nanomaterial-based gas sensors. A combination of the dry print transfer process for integration of NWs and a solvent-based technology for functionalizing NWs with NPs might be the method of choice for optimizing gas sensor devices.

CONCLUSION

In summary we evidenced that SnO_2 nanowires-based gas sensors produced by dry transfer process are sensitive to hydrogen sulfide. This print transfer method demonstrates high reproducibility and could be easily implemented as industrial fabrication approach. Thus the next step is to transfer metal oxide nanomaterials on CMOS-based devices involving dry transfer stamping method described in this paper. This is currently under progress.

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