Smart Materials

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This book of abstracts contains the results of the reports presented at the international workshop on Synchrotron Radiation and Smart Nanomaterials. The fields covered nano characterization of advanced materials using the large-scale infrastructure (synchrotron radiation centers), accelerated synthesis of novel functional materials, including microfluidic technologies, the results of supercomputer modeling, including machine learning. A separate section describes computer modeling and automation of the synthesis of biomedical materials.

Microfluidic synthesis of nanocomposites based on the BaGdF5 structure and the rare-earth metal-organic frameworks for application in X-ray photodynamic therapy

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Rare-earth nanocomposites for X-ray photodynamic therapy (XPDT) have been recently considered as an efficient alternative to conventional radiotherapy of cancer as well as contrast agent for CT imaging. The nanoscale composite typically consists of two components — a nanophosphor which re-emits X-rays into visible light that in turn is absorbed by the second component, a photosensitizer, for further generation of reactive oxygen species. Microfluidic synthesis of nanoluminophores made it possible to obtain nanocomposites based on BaGdF5 [1] and rare-earth metal-organic frameworks (RE-MOF) structures. The synthesized nanostructures can be used as X-ray activated XPDT system. The microfluidic synthesis of lumiphores enables faster synthesis while reducing the consumption of costly reagents. The BaGdF5 particles were obtained at 100°C for 6 minutes, compared to the traditional solvothermal method which required 24 h. Moreover, in situ flow measurements of the X-ray excited optical luminescence has been collected for the series of nanophosphors synthesis with varied flow rate of doping elements. The nanocomposite BaGdF5@RB was obtained by the one-stage microfluidic synthesis. Additionally, a series of RE-MOFs Zr0.7Gd1-xTbx-BDC-NH2 was also synthesised at 120°C for 30 minutes by microfluidic route.

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stage microfluidic synthesis route for BaGdF5:Tb3+ based nanocomposite materials: synthesis, characterization and bio-distribution. Int. J. Mol. Sci., 24, 17159 (2023).

New strategy for modeling of antiviral aptamers

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Currently, the search for new drugs for detection and combating viruses is actively underway. Aptamers are one of the promising compounds for these tasks. Recently, there has been a growing interest in the development of computational methods regarding approaches to aptamer selection. Previously, we proposed a scheme of a structure- and interaction-based design to create aptamers for RBD protein from scratch. As a result of in silico selection, two aptamers Apt27 and Apt31 were obtained and showed good binding with the target protein in both computational and experimental investigations. There is a need to significantly modify aptamer's tertiary structure to achieve blocking of a neutral top part of RBD. The main idea was to construct a new aptamer with two double helix stems and two loops which are separated by a single-stranded bulge. Negatively charged stems are supposed to interact with both positively charged side parts of protein, while nucleotides of the loops will provide specific binding and the bulge will cover the top part of RBD. To achieve the specific binding, we formed loops and the bulge by the same nucleotides as were in the loops of Apt27 and Apt31 aptamers. aptamer molecule volume is determined in the value of Vp = 35.28 nm^3, which corresponds to the molecular weight of DNA oligonucleotide MW = 27.55 kDa in the confidence interval of 25-29 kDa. Resulting aptamer showed antiviral properties in cell cultures and pseudo viruses.

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Building foundational model for XAS — universal E(3)-equivariant deep learning for on-the-fly prediction of X-ray absorption spectra

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X-ray absorption spectroscopy (XAS) is a widely used technique for determining the local geometric and electronic structure of matter. The experiment is usually performed at synchrotron radiation facilities, which provide intense and tunable X-ray beams. Samples can be in the gas phase, solutions, or solids.

We want to use the atomic structure of material as input into the model and get a spectrum with fixed photon energies as an output. So, we input cartesian coordinates of atoms to the model and the model outputs one-dimensional vector with absorption values. There are several robust deep learning methods for analyzing such data: Graph Neural Networks and Equivariant Neural Networks. The universality of the model regardless of the absorber atom was achieved by shifting all spectra to the same relative energy value. We used 32564 spectra of d-metals complexes with organic molecules calculated with full multiple scattering theory as training data and test data. The backward pass of the NN can be used further for the chemistry and XAS-informed structure refinement.

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Unravelling the structure-activity relationships of antioxidants: from good practices in machine learning to quantum chemistry and deep learning

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Antioxidants offer great opportunities for the design of new antineurodegenerative bioactive compounds. Antioxidants neutralize reactive oxygen species (ROS) and free radicals, which are unstable molecules that can cause cellular damage. By donating electrons to these radicals, antioxidants prevent oxidative damage to lipids, proteins, and DNA, thereby protecting cellular integrity and function. They also are used in drug formulations aimed at enhancing health outcomes by reducing oxidative damage associated with various pathological conditions. Despite that the QSAR and machine learning (ML) tools revolutionize other fields of drug development, ML for antioxidants remain unexplored topic.

Here we report the biggest known uniform (made by the same person in several years) database of molecular antioxidant activity and apply to it ML and deep learning. Moreover, molecular docking, graph neural network and quantum chemistry calculations further enhance the models performance upon the good practices from ML community.

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Pushing the boundaries of Small Angle X-ray Scattering with machine learning methods

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Protein crystallization is a time-consuming process that requires many trials and errors. The result of a crystallization experiment is not known in advance. To accelerate the process of obtaining protein crystals, machine learning (ML) methods can be used, which would allow predicting experimental outcome without waiting for the experiment to be finished. In our contribution, we employ machine learning models to predict experimental outcome based on small-angle X-ray scattering (SAXS) data, characterizing the protein solution hours after preparation.

The data regarding 56 crystallization experiments was used to showcase our approach. Two ML models were utilized – LogisticRegression (linear) and ExtraTreesClassifier (non-linear, ensemble). The SAXS curves from our dataset were smoothed and normalized and then were treated as input feature vectors for the models. Different features were derived from the original curves, including logarithm of the intensity and derivatives of the intensity. The training of the models was performed and the quality of prediction of the trained models was satisfactory (accuracy ~0.75). Analysis of different input features was conducted and the most informative regions and descriptors were determined.

To conclude, in our contribution we developed a new approach which has a potential to speed up significantly the research in the field of crystallization of biological macromolecules. We have shown that ML models are capable of reliably predicting the outcome of crystallization experiment based on SAXS data. In the future, we are going to apply our method to a larger dataset and also to generalize it to make trustworthy predictions for unseen molecules.

The synthesis of carbon-supported platinum nanoparticles in gas-liquid microfluidic system

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The use of microfluidics for the synthesis of metal nanoparticles has gained significant attention in recent years because of better mass and heat transfer, reagents' mixing and possibility to use extreme conditions as high temperature, high pressure and etc. [1] Also, microfluidic technology provides faster metal nanoparticles' synthesis process at lower temperatures comparing with batch synthesis, enhancing their functional characteristics [2,3].

We studied the effect of different parameters of the polyol synthesis on microfluidic setup using pressure and structural and morphological characteristics of resulting Pt/C samples and their electrochemical properties.

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MOFs as promising materials for food preservation technology

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Metal-organic frameworks (MOFs) have potential application in gas sorption, separation, storage, and release. The uptake of ethylene, a plant hormone, from atmosphere or the release of 1-MCP, an ethylene inhibitor, can be used to slow down the ripening process of fruits and vegetables. Here, we investigate the binding sites of ethylene and 1-MCP in $M_3(btc)_2$ structures by means of X-ray absorption spectroscopy, IR-spectroscopy and DFT simulations. The obtained XANES spectra of HKUST-1 sample with adsorbed ethylene, collected at laboratory source, correspond to Cu^{2+} sites, and were complemented by theoretical spectra to prove the adsorption of guest molecules. For the first time, in situ IR spectroscopy combined with theoretical simulations was used to obtain the three- dimensional structure of ethylene and 1-MCP bound to Cu-sites of HKUST-1 [1]. According to data from DRIFTS the peaks at 980 cm^{-1} and 668 cm^{-1} correspond to modes of adsorbed ethylene and 1-MCP in HKUST-1, respectively, and supported by theoretical vibrational spectra. Theoretical bonding energies screening was performed using B3LYP-D4 level of theory to find best candidates for ethylene/1-MCP storage/release among $M_3(btc)_2$ (M= Cr, Mn, Fe, Co, Ni, Cu, Zn) materials and compared with experimental values for $Cu_3(btc)_2$ [2].

The results demonstrated a good correlation between experimental and theoretical data in terms of adsorption geometries, binding energies and vibrational spectra [1] and shed light on ethylene and 1- methylcyclopropene binding in MOFs for application in food preservation technologies.

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Advanced fingerprint XAS analysis made simple: multielemental experimental libraries and machine learning in PyFitIt

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X-ray absorption near edge structure (XANES) spectroscopy is a powerful method to probe the oxidation state and local structure of metals in catalytic materials. However, it suffers from the lack of unbiased data analysis protocols. Machine learning (ML) overcomes human-related factors by uncovering relevant spectrum-structure relationships and subsequent cross-validation analysis. This work revises the classical XANES fingerprint analysis by database augmentation, feature extraction, cross-validation, and uncertainty analysis. We apply the developed methodology to decipher the oxidation state and local coordination of supported vanadium-oxo species (VOx), which change their structure participating in oxidative dehydrogenation catalysis. The developed library and instruments for analysis may serve as a starting point for a unified platform of fingerprint XANES data analysis.

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X-ray absorption spectroscopy - towards operando nanometrology

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The report provides an overview of the X-ray absorption spectroscopy applications at synchrotron radiation sources to determine the parameters of the nanoscale atomic and electronic structures of materials without long-range order in the arrangement of atoms. Particular attention is paid to the description of the machine learning application for analyzing big data of X-ray absorption spectroscopy both in the XANES and EXAFS energy regions to determine the parameters of the nanoscale atomic structure of materials based on theoretical analysis of experimental spectra. The peculiarity of this approach is that it allows not only to determine interatomic distances (radial distribution function) with high accuracy (up to 2 picometers), but also the angular distribution of atoms (chemical bond angles). The method opens the root for the determination of 3D local atomic structure parameters of any materials, including the possibility for studying the time-dependent processes.

A new approach is based on the development of methods for theoretical analysis of the fine structure of X-ray absorption spectra in three main energy ranges: pre-edge structure, XANES and EXAFS using machine learning technologies. The implementation of such a technique is important not only for expanding fundamental knowledge, but also for subsequent practical use. Based on the developed high-precision approach to materials diagnostics it is possible to create a metrological technique for determining the parameters of nanoscale local atomic and electronic structures of materials by the analysis of XAFS big data “on-the-fly” (during technologically important processes as well) and practically almost without human participation. The development of a method for X-ray spectral nanometrology is extremely important for solving the problems of accelerated development of advanced materials.

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A theoretical investigation of the structural characteristics and physical properties of aptamers

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The present study demonstrates the results of constructing the three-dimensional atomic structure of aptamer molecules in real solution conditions on the basis of small-angle X-ray scattering (SAXS) and comparison with X-ray diffraction (XRD) data. Theoretical modeling based on SAXS data yields satisfactory results, indicating that this approach is a promising avenue for obtaining the atomic structure of small molecules, which in turn can inform the design of new aptamers. The initial stage is the modelling of the secondary structures based on the nucleotide sequences. Subsequently, the actual full-atomic modeling of the 3D structure is performed based on the secondary structure. This offers an initial insight into the atomic structure of the aptamer and the spatial positioning of its principal structural components. Subsequently, molecular dynamics calculations are conducted on the aptamer, employing realistic physiological conditions. This provides information on the conformational changes of the aptamer in solution, with explicit consideration of the solvent, temperature, and pressure. Subsequently, quantum chemical calculations are conducted using the FMO method to refine the atomic structure obtained in the preceding step. Pairwise interactions are analyzed to elucidate the physical phenomena occurring between the aptamer and the protein. The theoretical scattering curves are then compared with the experimental SAXS scattering curves. This step is instrumental in selecting only those conformations of the aptamer that exhibit the least deviation from the experimental data.

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Pharmacology-informed high-throughput screening and generation of bioactive compounds via deep docking

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De novo drug design is a discipline, one of the tasks of which is to search for and develop drugs (in most cases, these are low molecular weight compounds) that could affect the components of signalling pathways that mediate the development of various diseases. [1]Generative models for images and language are becoming more and more widespread nowadays [2], but the scientific community faces an important question: is it possible to apply these machine learning methods in the field of creating new chemical compounds?

In this work, based on the several machine learning (ML) methods of molecular compounds generation and retrosynthesis, together with pharmacology-inspired filter rules (well-known Jorgensen, Lipinski et cetera) and deep docking, the big set of potentially synthesisable and bioactive compounds is generated and selected for the further synthesis.

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