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Wet Modification with Oxygen Storage Material of $NaFe_xPO_4$ as an electrode material for sodium-ion batteries

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Keywords: Sodium-ion batteries, Sodium iron phosphates, Ce modification, Electrode materials

Sodium-ion battery (SIBs) technology is one of the best promising alternatives to the lithium-ion batteries due to the low cost and abundance of sodium which are critical issues for large-scale application. One of the challenges facing SIBs is the exploration of new cheap electrode materials with efficient electrochemical performances suitable for practical applications. Among the sodium intercalation compounds, phosphate framework materials, and particularly these containing iron element ($Na_xFe_y(PO_4)_z$) have attracted increasing attention due to their low cost, safety and being environmental friendly. The intercalation-based cathodes typically rely on the cationic redox activity of the transition metals. The activation of both cationic and anionic redox reactions in the electrodes has been found to increase drastically the reversible capacity of P3-$Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ cathodes by using CeO_2 as an oxygen storage material. Moreover, first principle calculations have shown that anionic (O^{2-}) redox processes in $NaFePO_4$ are also visible.

Inspired by these data the main **idea** of the present contribution is to study the effect of Ce-modification on the electrochemical properties of $NaFe_xPO_4$ as cathode material in sodium and lithium half-cells. Ce-containing $NaFe_xPO_4$ has been prepared by wet modification process. The electrochemical properties of the phosphate cathodes containing different amount of Ce are studied in galvanostatic and potentiostatic regimes at 20 and 40 °C. The results show that the Ce-modification generates the following effects: (i) A change in the phase composition of $NaFePO_4$ with formation of NASICON and alluaudite type phases; (ii) Progressive increase in the redox potentials owing to the Fe^{2+}/Fe^{3+} pairs with increase in the Ce amount; (iii) Strong polarization of both Na- and Li-ion cells which causes the capacity drop during the cycling; (iv) Ce-modification is beneficial for high-temperature operation (40 °C) of the Li cells: the smaller Ce amount increases the specific capacity, while the larger amount is beneficial for the stable cycling. From these data one can conclude that further electrode optimization will enable to overcome the strong polarization of the ion cells and, hence to improve the electrochemical performance of the Ce-modified $NaFe_xPO_4$ electrodes.

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Effective approaches for enhancing electrochemical performance of layered $NaTMO_2$ oxides

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Keywords: layered oxides, bulk and surface modification, sodium-ion batteries, sustainable energy storage

Among all positive electrode materials for sodium-ion batteries, the sodium transition metal oxides ($NaTMO_2$) with layered structure are in practical interests. However, these types of oxides have not yet reached their optimal electrochemical properties in terms of specific capacity and cycling stability.

Within the framework of the CARiM project, over the last few years, we have developed several different and effective approaches to improve the electrochemical performance of these electrode materials. One of the approaches we have adopted is to stabilize the bulk of the P*3*-$Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ structure by introducing electrochemically inactive ions, i.e. Mg^{2+} and Ti^{4+} ions were used through partial replacement of low- and high-oxidized nickel ions, respectively: $Na_{2/3}Ni_{1/3}Mg_{1/6}Mn_{1/2}O_2$ and $Na_{2/3}Ni_{1/3}Ti_{1/6}Mn_{1/2}O_2$ [1,2]. Furthermore, the metal-substituted oxides were surface modified by an oxygen storage material, such as CeO_2 [3,4]. The results show, that Ti-substituted oxide displays moderate cycling stability and poor rate capability [3,4]. Contrary to Ti^{4+}, the Mg^{2+} substituents mainly influence the nickel redox activity and suppress the deposition of MnF_2, all of them contributing to the exceptional cycling stability and rate capability [2,3,4]. The CeO_2 modifier has a much stronger effect on the oxygen redox activity than that of metal substituents; thus, the highest specific capacity is attained [3,4].Taking into account these results, in the next stage we modified the surface of $Na_{2/3}Ni_{1/3}Mg_{1/6}Mn_{1/2}O_2$ with another electrochemically inactive oxides, i.e. Al_2O_3. It is found that better electrochemical performance is achieved, in terms of specific capacity and cycling stability, when Al_2O_3 is used instead of CeO_2.

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Effect of the CeO_2 coating on electrochemical performance of layered oxide cathode with composition $Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$

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Keywords: layered oxides, CeO_2 coating, oxygen activity, cathode material

The layered materials provide a combination of high capacity, high voltage, and high stability and are widely studied in attempts to develop new cathode materials for sodium-ion batteries. The variety of existing layers' arrangements opens potential for diversity in their properties, including their performance as an energy storage material. One of the candidates for a cathode material that crystallizes in P2 and P3 phases is a layered oxide, $Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$, characterized by charge-discharge capacity provided by $Mn^{4+/}Mn^{3+}$ redox couple in a voltage range below 4.0 V and by O^{2-}/O^{-} redox couple at a voltage above 4.2 V.

The achievement of enhanced electrochemical performance by extending the upper voltage boundary leads to deterioration of the cathode surface layer, due to interfacial or surface reactions. The evolution of the interface depends on the active material composition and the nature of the electrolyte. Applying a cathode coating could reduce surface degradation of cathode and ensure a smoother surface. A variety of coating materials were studied, such as Al_2O_3, ZrO_2, ZnO, CeO_2, etc.

In this study, CeO_2 was coated on the surface of $Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$ particles (existing as P2 and P3 phase) via ethanol-assisted homogenization with $Ce(CH_3COO)_3$, until the ethanol evaporated. The dry precipitate is heated respectively at 600°C (for the P3 phase) and 800°C (for the P2 phase) and is used for cathode active mass preparation. The selection of CeO_2 as a coating material is due to its high oxidation capacity, which originates from the rapid shift of the oxidation state between Ce^{3+} and Ce^{4+}. Resorting to CeO_2 coating in layered oxide materials aims to improve oxygen storage and stabilize layered structure.

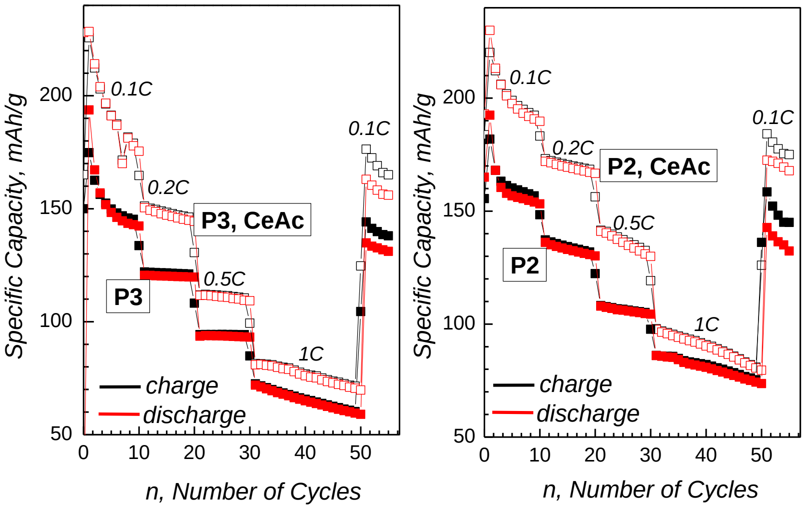

Fig.1. Cycling performance of pristine P3 and P2 phase ($Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$) and of P3 and P2 phase coated with CeO_2.

The surface-modified cathode materials show distinctively better electrochemical performance than corresponding pure phases. The effect of CeO_2 coating was further studied by ex-situ XRD, EPR, and SEM analysis of cathode material.

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Graph-Theory-Based Prognosis of Electrolyte Degradation Products in Lithium- and Sodium-Ion Batteries

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Keywords: electrolytes, metal-ion batteries, graph theory

The growing demand for sustainable energy storage devices requires fabrication of novel materials for rechargeable batteries. The stability of the electrolytes in the electrochemical cells plays a pivotal role for the cycling stability of the energy storage devices. The processes taking place inside such systems are fairly complex and hence the identification of unwanted side reactions affecting the electrochemical stability is not trivial.

The present study utilizes graph theory and quantum chemistry to develop an algorithm capable to generate diverse viable side products of redox reactions that a given electrochemical system, can undergo. Two case studies of electrolyte degradation are presented: namely, ethylene carbonate (EC) and diglyme (DG). The effect of the electrode surface is modeled implicitly by taking into account the possibility of electrolyte solvent dehydrogenation reactions. The predicted degradation products after reduction and oxidation are validated against previously reported experimental data.

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Electrode-electrolyte Interface in Metal-ion batteries – a Stage for Intriguing Passions

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Keywords: Hybrid metal-ion batteries, DFT, Dual-cation electrolyte, Lithium titanate electrode

Nowadays, the humankind is grossly dependent on batteries in all aspects of its activities. Currently, the Li-ion batteries are doubtlessly the most widely used ones but cost and safety issues inspire the testing of other metal ions as charge carriers. Another approach is the creation of hybrid-ion batteries, but this requires the design of new electrode and electrolyte materials. Of particular interest are the processes occurring at the electrode-electrolyte interface, since they are critical for the operation of the device in terms of rate and efficiency. Quantum-mechanical modeling is a powerful tool for investigation of these processes at the molecular level. The objective of our study is to evaluate the desolvation energetics of light metal cations in the presence of electrode surface. In our models the electrode surface is the oxygen terminated (111) face of $Li_4Ti_5O_{12}$ (LTO) – a widely studied electrode material possessing numerous advantages. The electrolytes are individual or mixed salts of Li^+, Na^+ and Mg^{2+} neutralized by PF_6^- ions in ethylene carbonate as solvent. Periodic calculations were performed with PBE/PAW method as implemented in VASP; isolated ion-solvent clusters we treated at the B3LYP/6-31G*/SMD level with Gaussian 16. Comparison is made of the desolvation behavior on the surface, in vacuum, and in implicit solvent. The results show an intermediate desolvation propensity at the surface in comparison to vacuum and implicit solvent. The results are discussed in the light of experimental findings, connecting electrolyte surface decomposition with gassing in LTO-electrode cells.

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Design of Bipolar Organic Matrices for Reversible Redox Reactions in Non-Aqueous Electrolytes

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Keywords: Organic electrode materials, diselenolo-substituted naphthalimide, DFT

Organic electrode materials (OEMs) combine high-energy density with cost-effectiveness and environmental compatibility which makes them currently a target of intense research. Depending on the ease of reduction and oxidation, OEMs are used either as cathodes or as anodes in metal-ion batteries but the bipolar OEMs contain both reducible and oxidizable fragments and thus can serve as symmetric electrodes.

Naphthalimide derivatives occupy a special place among OEMs due to their intriguing redox–switchable properties. Recently, peri-disulfo derivatives were synthesized and tested as successful bipolar OEMs for Li-ion batteries [1]. Given that selenium is a better nucleophile than sulfur, peri-diselenolo analogues were designed and their implementation in electrochemical cells with LiTFSI in ionic liquid as electrolyte was analyzed both experimentally (by ex-situ XRD, SEM/EDS and EPR analyses) and computationally (by means of molecular modelling with DFT) [2]. Structural, electronic and electrochemical characteristics were quantified to supplement and interpret the experimental findings. Comparison with the performance of previously designed coordination polymers is made.

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Redox reactions in symmetric electrochemical cell for sodium-ion batteries

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Keywords: Na-ion batteries, Symmetric cell, DFT

One of the main challenges concerning the safety of sodium-ion batteries (SIBs) is to ensure complete compatibility between the electrolyte and the electrodes. The electrolyte must have high ionic conductivity, a wide electrochemical stability window and chemical stability with respect to the other components in the battery. A mixture of propylene carbonate (PC) and $NaPF_6$ meets these requirements. On the other hand, electrode materials must have a high specific capacity and be inert to the electrolyte. Layered oxides of sodium and transition metals are often used as cathodes in SIBs. The aim of the present study is to investigate the stability of a sodium electrolyte with a composition of 1M $NaPF_6$ dissolved in PC against the layered oxide $Na_{0.67}Ni_{0.5}Mn_{0.5}O_2$ at high electric potentials. The electrochemical stability window of the sodium electrolyte was determined by linear voltammetry using symmetric ion cells. Partial decomposition of the electrolyte was observed at threshold values of the electrical voltage, the products of which were identified by in-situ electron paramagnetic resonance (EPR) in combination with quantum chemical calculations with Density Functional Theory [1]. The electrode material $Na_{0.67}Ni_{0.5}Mn_{0.5}O_2$ was prepared by solid state reaction between co-doped nickel-manganese carbonates with sodium carbonate at high temperatures. This synthetic approach allows the spherical morphology of the carbonates to be preserved in the target oxide products. The influence of the oxide electrode on the chemical reduction and oxidation pathways of the electrolyte was investigated by the usage of a symmetric cell methodology. This effectively allows to monitor the interaction between the cell components without involving unwanted side reactions. The electrochemical characteristics of the cell such as capacity, cycling stability and reversibility are promising. Based on the obtained results, possible sodium electrolyte decomposition reactions initiated by the oxide electrode are proposed.

Acknowledgements: The financial support is from CARiM/Vihren, grant KP-06-DV-6/2019

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Dry Coating modification with CeO_2 of $Na_4Fe_3(PO_4)_2P_2O_7$ as promising electrode material for sodium ion batteries

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Keywords: Sodium-ion batteries, CeO_2 modification, Dry coating, Electrode materials

For practical applications of sodium ions batteries (SIBs), energy density, in addition to rate capability, is one of the most important characteristics of the electrode materials. The mixed phosphate-pyrophosphate, $Na_4Fe_3(PO_4)_2P_2O_7$ (NFPP), is considered to be the most attractive cathode material for large scale applications owing to its low cost, natural abundance and reasonable energy and power density. One of the approaches to improve its poor cycling and rate performance is coating with various carbon conducting materials, usually about 10-15 wt. %. Such a large amount of carbon, together with added carbon black and binder, decreases significantly the volumetric energy density of the cathodes, since the carbon is inactive and bulky. In this aspect, the use of other conductive additives or modifiers in very small amounts instead of carbon can provide a high volumetric energy density, but this faces huge challenges.

In this study, we have explored as sodium cathode materials composites NFPP containing only 1 wt.% CeO_2 as a conductive additive, the latter being obtained by two different ways. The composites are prepared by a simple dry coating method. The electrochemical tests in Na half-cells are performed in potentiostatic and galvanostatic modes using two sodium electrolytes (**Fig. 1**).

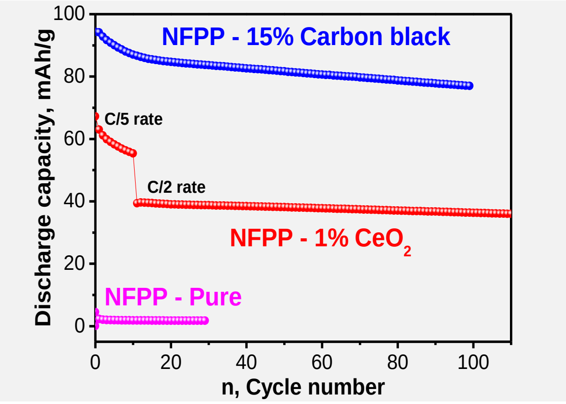

Figure 1. Comparison of the cycling stability at C/2 rate of NFPP-pure, NFPP-coated with 1 wt.% CeO_2 and NFPP-coated with 15 wt.% carbon black ($NaPF_6$ in PC electrolyte)

The results obtained show: (i) Coating NFPP with even 1 wt.% CeO_2 leads to a drastic increase in the specific capacity of the cell with good cycling stability and 100 % Coulombic efficiency in comparison with pure NFPP; (ii) The specific capacity of NFPP coated with 15 wt.% carbon black is higher, but at the expense of the significantly decreased volumetric energy density.

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Influence of cerium (IV) oxide for reversible oxygen activity in Li_2RuO_3 and Li_3RuO_4

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Keywords: lithium-ion batteries, lithium ruthenate, cerium dioxide, redox activity of oxygen

Introduction – ruthenates are group of inorganic compounds with variety of oxidation states of ruthenium ranging from plus (IV) to (VII). That rich variety of oxidation states combined with layerd structure makes them highly perspective for use of battery applications. A very high specific capacity for some of these compounds has been reported [1,2]. This is possible because two different forms of active redox reaction affecting both the transition metal and the oxygen are possible. Our main objective is to activate the oxygen redox activity which can significantly enhance the specific capacity of ruthenate based electrode materials to above 300 mAh/g. Achieving such a high specific capacity poses a challenge because the oxygen activity becomes irreversible shortly after few cycles and hence oxygen gas is relessed into the battery enclosure and a serious decrease of specific capacity is observed. In the present work we study the influence of the irreversible oxygen activity. We hypothesize that addition of cerium (IV) oxide to ruthenate based electrode materials can influence the irreversible oxygen activity by reversibly binding during battery charging and releasing oxygen during the discharge phase. The modification of ruthenates with CeO_2 is motivated due to its exceptional capability to store oxygen reversibly.

Experimental - high temperature solid state reaction is chosen for preparing the Li_2RuO_3 and Li_3RuO_4 for pure samples. For the CeO_2-modification, a combined method including co-precipitation of cerium (III) on the ruthenate surface followed by high temperature calcination in oxygen rich atmospehere is developed. The electrochemical characterization of oxides was carried out in half lithium-ion cell using lithium electrolyte containing 1M $LiPF_6$ solution in EC:DMC.

Results and Discussion – the specific capacities of the ruthenates were determined using galvanostatic cycling with potential limitation (GCPL). Figure 1 presents the charge-discharge curves of CeO_2-modified Li_3RuO_4. The data show that the modified oxide delivers a reversible capacity of around 250 mAh/g, which is close to the theoretical ones (i.e. 288 mAh/g corresponding to 2 mol Li^+). After modification, the reversible capacity remains stable during cycling in a wide potential range (i.e. between 1.5 and 4.2 V). Structural changes of oxides during cycling was monitored by ex-situ X-ray diffraction (XRD), wile the variation in the oxidation states of paramagnetic ions was accessed by ex-situ electron paramagnetic resonance spectroscopy (EPR).

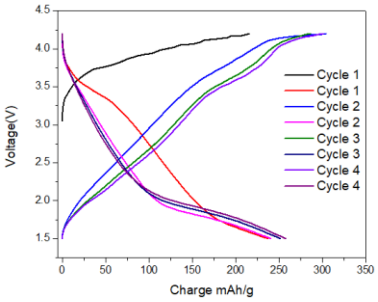

Figure 1. : GCPL of Li_3RuO_4/CeO_2 5%

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Molecular Modelling of Hard Carbon Anode Materials for Sodium-Ion Batteries

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Keywords: hard carbon, DFT, DFTB, sodium-ion batteries, van der Waals correction, Na clusters

In recent years, research has increasingly focused on alternative chemistries to Li-ion batteries, collectively referred to as post-lithium systems. Sodium stands out as a promising choice due to its abundance and low cost. However, graphite is not a viable anode material in Na-ion batteries because of its poor sodium storage capacity. In contrast, hard carbon (HC) offers excellent sodium intercalation behavior. A key benefit of HC is its sustainable origin, as it can be obtained from low-cost biomass waste such as leaves, nutshells, and cork. The structural features of hard carbon—namely, short-range graphitic domains, sp^3-carbon linkages, and porosity—depend on the precursor, pyrolysis conditions, and heteroatom content. In this work, we investigate representative HC structures incorporating conjugated carbon motifs (CCMs) and evaluate their electrochemical properties using both the Density Functional Theory (DFT) and the Density Functional Tight Binding (DFTB) method. Our results show that DFTB is a computationally efficient alternative for screening conformers, successfully capturing energy trends. Nonetheless, DFT remains essential for complex systems. We also explore the role of inclusion of van der Waals corrections and the influence of electron donating and withdrawing groups on sodium insertion potential and capacity. Cluster simulations reveal a shift from Na/substrate interactions to sodium aggregation as Na concentration increases.

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Possibilities of the total reflection X-ray fluorescence technique for analysis of fluid inclusions in galena crystals

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Keywords: Galena; Fluid inclusions, Synthetic solution, TXRF analysis

Some galena crystals from the Madan Ore District, formed under boiling conditions, contain unique microliter-sized gas-liquid inclusions. The analytical characterization of these inclusions could reveal valuable information on the composition of mineral-forming solutions and the presence of specific rare element-indicators, thus facilitating the study of crustal rock evolution.

One possibility for rapid quantitative multielement analysis of such µL -volume samples, with elemental compositions across a wide concentration range (from per cent to sub-ppm levels) is provided by the total reflection X-ray fluorescence (TXRF) technique. By simply piercing the inclusion membrane, marked by a slight depression on the crystal wall, the liquid phase can be collected, weighed, and analyzed by TXRF, enabling a direct evaluation of the bulk salinity.

The first step in such investigations is the step-by-step optimization of the analytical procedure using a multielement synthetic fluid inclusion analogue. In this study, a custom laboratory standard, Synsol, containing chlorides of Na, K, Ca, Fe, Mn, Cu, Zn, Pb, Rb, and Ba, was prepared and analyzed by TXRF, with Ga used as an internal standard. To determine optimal conditions for analysis, various µL- aliquots of Synsol were diluted with ultrapure water to final volumes ranging from 0.2 to 1 mL. A Ga standard solution was added to each dilution, resulting in a final concentration of 1 mg L^{-1} Ga. After homogenization, 5 µL of each mixture was pipetted onto acrylic glass disks and dried under an IR lamp. This pipetting and drying procedure was repeated three times to ensure uniform deposition. The samples were then measured with an exposure time ranging from 100 to 1000 s using the S2 PICOFOX 400 (BRUKER Nano GmbH, Germany) instrument.

The best correspondence between the prepared composition and the analytical results was found for a dilution of 10 µL aliquots of Synsol to 1 mL and an exposure time of 500 s. For smaller aliquots, dilution to 0.2 mL also provides good agreement. In conclusion, TXRF proved to be a fast and simple microanalytical method for the simultaneous determination of various elements in fluid inclusions, with concentrations ranging from percent levels to trace amounts.

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XPS Study of Zink and Titanium Mixed Metal Oxides Obtained by Magnetron Sputtering

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Keywords: Magnetron sputtering, XPS, metal oxides.

Magnetron sputtering (MS) is a technique that is widely used for the deposition of metal and oxide films with controlled crystal structure and surface roughness, suitable for sensor element applications.

The present study is focused on the synthesis and characterization of mixed metal oxides for gas sensor applications. ZnO-TiO_2 composite thin films were deposited on silicon substrates by MS technology in an argon atmosphere.

X-ray photoelectron spectroscopy (XPS) is one of the most widely used **surface analysis** techniques due to its extremely **high surface sensitivity.** The XPS studies were performed **using** a VG ESCALAB II system with AlK_{α} radiation. It was employed to perform a qualitative and quantitative analysis of the elements. The analyses showed that the surface of the samples contains C, Zn, Ti and O elements. The concentration of the elements on the surface was determined and it was established that the resulting films are dense and homogeneous. From the calculated concentrations it was observed that by varying specific parameters during the simultaneous magnetron sputtering of Zn and Ti in an argon atmosphere, different Zn/Ti ratios can be achieved.

To determine the chemical state of the zinc, in addition to measuring the binding energy of the Zn 2p peak, the Auger Zn LMM XPS spectra were analyzed and the modified Auger parameter was calculated. It was found that both metallic zinc and ZnO form are present on the surface. Analysis of the results obtained from the Ti 2p spectrum revealed the presence of metallic titanium and various forms of titanium oxide. The presence of oxygen vacancies and oxygen-containing species adsorbed on the surface was identified, which suggests the potential application of these layers in gas-sensitive elements.

It was found that magnetron sputtering from metallic targets (Zn and Ti) in an argon atmosphere leads to the deposition of metals, which are likely oxidized upon exposure to air. The results of the research show that mixed oxides of ZnO and TiO_2 can be synthesized in a controlled manner by magnetron sputtering, using appropriate sputtering parameters.

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New Materials for Semiconductor Gas Sensors Prepared by Vacuum Evaporation and Magnetron Sputtering

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Keywords: vacuum evaporation, magnetron sputtering, gas sensors

The materials intended for the manufacture of semiconductor gas sensors are very attractive due to the need to detect ever smaller concentrations of CO, nitrogen oxides and hydrocarbon emissions. They must meet many requirements, based on their sensitivity, selectivity, reversibility, response time, and long-term stability. For this reason, both the type of elements from which they are made and the method of their preparation are of particular importance for their efficiency. It influences parameters essential for their operation – morphology, surface size, chemical state of the elements, presence of impurities, etc.

Thin copper films on a silicon substrate have been obtained by vacuum evaporation. They are intended for manufacturing of the interdifited electrodes of the sensor electrodes of semiconductor gas sensor elements. Magnetron sputtering have been used to form the sensor material of the electrodes. The resulting sensor materials are based on aluminum nitride and chromium – titanium. The films have been characterized by XPS, GDOES (Glow Discharge Optical Emission Spectroscopy), XRD, SEM. The results of XPS studies show that a layer of metallic copper have been successfully deposited by vacuum evaporation. Sensor coatings of AlN and Cr-Ti have been also successfully formed by magnetron sputtering. The formation of phases of copper, AlN and Cr-Ti have been also confirmed by XRD analyses. The performed depth analyses by GDOES of AlN confirmed the results of XRD analyses that AlN have been successfully formed. GDOES of Cr-Ti showed a uniform distribution of elements in depth. SEM analyses showed that the obtained films have a highly developed surface and are suitable for use as sensor materials.

The analyses have shown that vacuum evaporation and magnetron sputtering, compared to other widely used methods for their preparation, are extremely promising methods for the production of semiconductor gas sensor elements.

Acknowledgements: The authors are grateful to the project КП-06-Н87/8 "Development of sensor elements based on composite metal-oxide thin films and nanostructures", funded by the National Science Fund, Bulgaria for the financial support to realize these investigations.

Luminescent properties of Dy^{3+} doped and Dy^{3+}/Eu^{3+} co-doped $50ZnO.40B_2O_3.5WO_3.5Nb_2O_5$ glass

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Keywords: glasses, rare earths; photoluminescence

Rare earth – doped glasses are widely studied as luminescent materials due to their visible emission, high thermal stability, relatively easy fabrication and possibility of obtaining large bulk samples compared to crystals. Among oxide glasses, binary ZnO - B_2O_3 glasses have been attracting continuous scientific interest, due to their high transparency from the visible to mid-infrared region of the spectrum, a relatively low melting temperature, and good chemical and thermal stability.

Four component glasses with the compositions of $50ZnO.40B_2O_3.5WO_3.5Nb_2O_5.xDy_2O_3$ (x=0, 0.25, 0.5, 0.75, 1 mol.%), $50ZnO.40B_2O_3.5WO_3.5Nb_2O_5.0.5Dy_2O_3.xEu_2O_3$ (x=0, 0.25, 0.5, 0.75, 1 mol.%) were obtained by applying the melt-quenching method.

It was established that the addition of WO_3 and Nb_2O_5 to the zinc borate glasses leads to improvement of the emission properties of the active ions through the occurring non-radiative energy transfer from the tungstate and niobate groups.

Moreover, energy transfer from Dy^{3+} to Eu^{3+} active ions is also observed and confirmed by the fact that in the co-doped glasses intensity of the Dy^{3+} transitions decreases progressively with increasing Eu^{3+} concentration, while the intensity of Eu^{3+} emission bands increases. These facts show that $50ZnO:40B_2O_3:5WO_3:5Nb_2O_5$ glass matrix is suitable for hosting both active ions and can serve as host sensitizer.

Depending on the rare earth doping content, the researched glasses may be used as orange light emitting materials. The CIE coordinates may be modified by altering the dopant ratio and the obtained color shifted from yellow-orange to dark orange light region.

Acknowledgements: Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by the Bulgarian Ministry of Education and Science.

Trace Metals Bioavailability in River Waters Affected by Mining Activities in Bobov Dol Region

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Keywords: bioavailability, chemical equilibrium models, chemical species

The bioavailability of elements is related to the presence of chemical species, mainly free ions or labile inorganic species, that can interact with biological systems, causing them to have a toxic or beneficial effect. Thus, the bioavailability of trace metals in natural surface water depends on their chemical species distribution and the physicochemical and chemical water characteristics. The approach we applied was to combine physicochemical and analytical measurements with chemical equilibrium models that enable the quick and accurate acquisition of information about the metal chemical species as an indicator of their bioavailability.

The bioavailable species of the most common pollutants in water affected by coal mining and processing - Cu, Zn, Cd and Pb were evaluated in two rivers located near the Bobov Dol mine and the Bobov Dol thermal power plant (TPP) - Babinska and Razmetanitsa. The physicochemical parameters and the total concentration of the elements are used as input data for thermodynamic calculations. The distribution of Zn, Cu, Cd and Pb chemical species and their variation with the changes of pH, DOC and alkalinity in the studied water bodies were calculated using two chemical equilibrium models - combined ion-association - Stockholm humic model (IA-SHM) and biotic ligand model (BLM).

The both models showed similarity in the calculated Zn, Cu, Cd and Pb species. Insignificant amounts of free Cu^{2+} and Pb^{2+} ions were calculated, which points to their low level of bioavailability. In contrast, dominant free Zn^{2+} and Cd^{2+} ions were calculated in most of the investigated water, which makes them riskier than Pb for aquatic organisms despite their low concentrations. Unlike Cu, calculations for Pb and Cd by both models and for Zn by IA-SHM showed a tendency of decrease in free ions, respectively a decrease in bioavailability with increasing pH and DOC and with decreasing alkalinity.

Despite the similarities in the calculations for both models, there are significant differences in the distribution of species in Zn and Cd and insignificant ones in Cu and Pb. For Zn, the amount of free Zn^{2+} ions calculated by BLM is by 17-20 % lower than that calculated by IA-SHM. For Cd, 10-20% carbonate species were calculated by IA-SHM, which are absent in the calculations with the BML. We explain these differences with the mutual competition of metals accounted for by IA-SHM and consider that IA-SHM is more effective than BML for assessing the bioavailability of trace elements.

Phase constitution in intermetallic Ti-Al-Nb-based alloys

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Keywords: TiAl-based alloys, microstructure, transmission electron microscopy (TEM)

Intermetallic titanium aluminides are considered for high-temperature applications in the aviation and automotive industries due to their potential of significant component weight saving in combination with high-strength and good creep properties. TiAl-based alloys have proven to be capable to replace Ni-based superalloys at temperatures up to about 800°C in applications such as, e.g., turbine blades in aero-engines. One of the major problems of these TiAl-based materials is their poor formability at high temperatures. A significant improvement is achieved by the addition of Mo or W to the Ti-Al-Nb alloy system which is one of the basic systems for the currently used alloys. In order to improve the existing alloys and their processing characteristics further alloy development is required. To achieve this goal, an exact knowledge of the phase equilibria and phase transformations at elevated temperatures is needed, as a pre-requisite for microstructure control to adjust the high-temperature mechanical properties. Primary results of the microstructure of two investigated alloys with composition Ti-32.1Al-11.1Nb-3.7Mo and Ti-32.3Al-12.35Nb-1.2W (at. %) are presented.

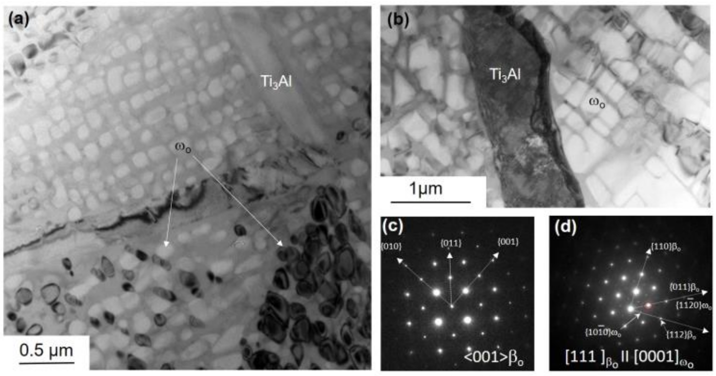

Fig.1 (a) TEM image of Ti-32.1Al-11.1Nb-3.7Mo alloy taken near $<001>_{\beta_o}$, (b) TEM micrograph of Ti-32.3Al-12.35Nb-1.2W alloy taken near $<001>_{\beta_o}$, (c) SAD acquired along the <001> zone axis and (d) SAD acquired along the <111> zone axis of β_o in the Ti-32.1Al-11.1Nb-3.7Mo alloy.

The microstructure of both alloys shows large β_o grains with α_2-Ti_3Al as laths inside and homogeneously distributed ω_o precipitates within the β_o matrix. As seen in these TEM micrographs (Fig. 1a,b), precipitates up to 200 nm in size are uniformly distributed in the matrix. The selected area electron diffraction (SAD) pattern reveals the ordered structure of β phase and an orientation relationship between the two phases. Some of the ω_o precipitates exhibit different contrast due to various orientation variants. The cuboidal shape without misfit dislocations (confirmed by HRTEM analysis) indicates that the precipitates/matrix interface is coherent with a high misfit strain.

Optical characterization of Cr^{4+} doped Li_2CaGeO_4 transparent glass- ceramic

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Keywords: Spectroscopy; Optical properties; Lifetime; Glass ceramics

We present the synthesis and optical characterization of Li_2CaGeO_4: Cr^{4+} glass-ceramic. A systematic investigation was made to choice the optimal initial glass composition from the Li_2O-CaO-GeO_2-B_2O_3 system and the optimal thermal treatment conditions to obtain the glass-ceramic. The glass-ceramic possess several characteristics such as, i) 18-24 nm size of the nanoparticles and about 60 wt % Li_2CaGeO_4: Cr^{4+} nanoparticles concentration in the glass, and ii) good transparency. The optical measurements and calculations show that Cr^{4+} experiences a medium-strength crystal field (Dq/B =2.0) near the cross-point of the energy levels $^3T_2$ and ^1E. Dq/B values for different compounds are compared and discussed. Intense transition of excited electrons between the $^3T_2$ and ^1E levels is observed. As a final result, wide optical emissions from 1100 to 1500 nm, centered at 1215-1250 nm and lifetime around 40 µs were obtained. This lifetime achieved for Li_2CaGeO_4: Cr^{4+} glass-ceramic is significantly longer than the values for the well-known Cr^{4+} doped forsterite and garnet (about 5 µs). It is comparable with the lifetime of some silicate glass-ceramic, but their production is more complicated because of the higher temperature for the initial glass preparation.

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Active Sites in Sulfated Zirconia: Insights from Isotope Exchange and FTIR Spectroscopy

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Keywords: Probe molecules; Sulfate coordination; CO; acetonitrile; adsorption

Sulfated zirconia (S-ZrO_2) is a well-known material widely used in catalysis, yet the coordination of sulfate groups and accessibility of active sites remain topics of ongoing discussion. In this study, we applied FTIR spectroscopy with isotope substitution (^{16}O/ ^{18}O in sulfate groups) and probe molecules (CO and CD_3CN) to investigate the coordination environment and surface acidity of sulfated tetragonal zirconia. Isotopic substitution caused a uniform shift in the SO_4-related IR bands without splitting, indicating tridentate coordination of sulfate groups in the activated state. Upon hydration, a distinct shift in band position suggested a change to bidentate coordination. These coordination changes were further supported by probe molecule adsorption. CO was only adsorbed on S-ZrO_2 after thermal activation, implying that the Zr sites are accessible when sulfate is tridentately coordinated. In contrast, CD_3CN, a stronger base, was adsorbed both in the hydrated and activated states. This behavior indicates that in the hydrated material, bidentate SO_4 groups coexist with Zr sites coordinated to terminal OH groups, which block CO adsorption but can be displaced by acetonitrile.

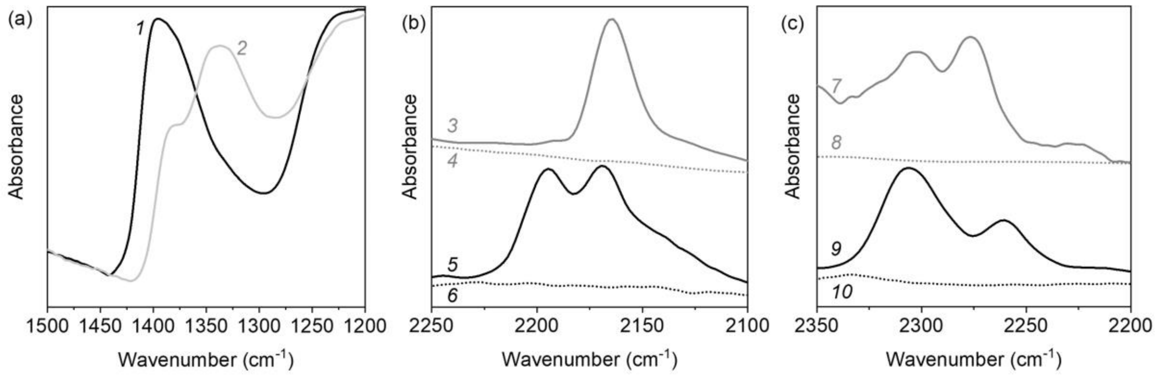

Figure 1. (a) FTIR spectra of the S-ZrO_2 sample after evacuation at 470 °C (spectrum 1) and after $^{16}O/^{18}O$ isotope substitution in sulfate groups (spectrum 2). (b) FTIR spectra of the S-ZrO_2 sample before (dotted lines) and after (solid lines) CO adsorption. The sample was pre-evacuated at either 25 °C (spectra 3 and 4) or at 450 °C (spectra 5 and 6). (c) FTIR spectra of the S-ZrO_2 sample before (dotted lines) and after (solid lines) exposure to 1 mbar of CD_3CN. The sample was pre-evacuated at either 25 °C (spectra 7 and 8) or 450 °C (spectra 9 and 10).

In conclusion, our findings highlight the dynamic coordination behavior of SO_4 groups on ZrO_2 and provide new insights into the relationship between sulfate coordination, hydration state, and active site accessibility, crucial for understanding and optimizing sulfated solid acid catalysts.

Acknowledgements: Research was financially supported by the Bulgarian Science Fund (grant number КП-06-ДВ-1).

Study of Pr_6O_{11} as a potential substitute of CeO_2 in lithium-ion batteries

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Keywords: lithium-ion batteries, lithium ruthenate, praseodymium oxide, oxygen peeling

Cathode materials determine the energy density and the cyclic stability of Li-ion batteries. Because of that, transition metal oxides undergo active research. Traditional cathode materials rely on reversible lithium intercalation. The usage of 4d-metals in high oxidation states increases material’s energy density. Li_2RuO_3 has reversible capacity due to 2-electron Ru(VI)/Ru(IV) shifts. [1] The material`s main disadvantage is irreversible release of oxygen which permanently reduces capacity. To counter such processes, finding substances with reversible absorption of oxygen. A classic example is CeO_2, however research of suitable alternatives is lacking. Lanthanides give two candidates: Pr_6O_{11} and Tb_4O_7. Praseodymium oxide has successfully shown catalytic and electrochemical properties with promising results. The activation of one-electron Pr(III)/Pr(IV) shift in the process of electrochemical cycling of the cell, allows reversible oxygen absorption, analogous to cerium oxide. This led to the study of our electrode system, Li_2RuO_3 + 5% Pr_6O_{11}.

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Cycling voltammetry study of 1,8-substituted naphthalimides with Li$^+$ and Na$^+$ ions in a non-aqueous media

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Keywords: 1-8 naphthalimides; bipolar organic materials; cyclic voltammetry; *n*- and *p*-type redox reactions

Environmental pollution and depletion of natural resources have always been major problems that humanity has been striving to solve. With the technological advancement and the widespread use of lithium-ion batteries in our daily lives, the need to search for more environmentally friendly and potentially cost-effective alternatives has come to the fore. Organic rechargeable batteries can be the successors of LIBs as next-generation energy storage systems due to the flexibility of organic design, environmental friendliness, etc.

This report presents the redox interaction of bipolar organic matrices with Li$^+$ and Na$^+$ ions. The compounds were investigated electrochemically by cyclic voltammetry in non-aqueous electrolytes. Cyclic voltammetry shows that the Se-substituted compounds participate in *n*- and *p*-type redox reactions at around 2.0 V and above 4.0 V vs. Li/Li$^+$, respectively. At lower potentials, Se-substituted compounds are able to take up to 6 Li$^+$ ions, depending on the type of electrolyte used. The results for Se-substituted compounds are compared with data for S-substituted ones.

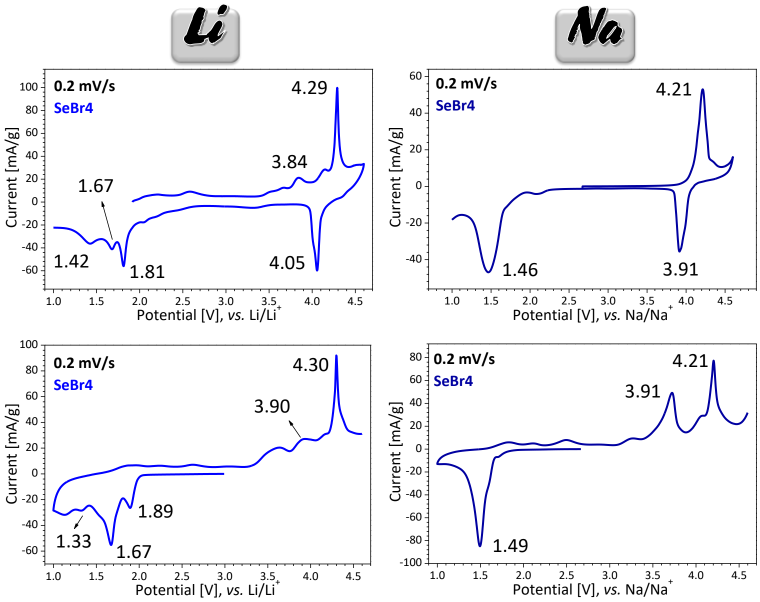

Figure 1. CV curves of **SeBr4** used as electrodes in model three-electrode electrochemical cells against Li in 1M LiTFSI-Pyr$_{1,3}$FSI and Na in 1M NaFSI-Pyr$_{1,3}$FSI started with cathodic and anodic scans, respectively.

Acknowledgements: The Bulgarian National Science Fund funded this study under grant number КП-06-H69/1 (8.12.2022). The electrochemical experiments were performed on equipment provided by the project BG05M2OP001-1.001-0008 "National Centre of Mechatronics and Clean Technologies", funded by the Operational Programme Science and Education for Smart Growth, co-financed by the European Union through the European Regional Development Fund.

Morphology of Metal-Oxide Nanostructures Produced by PLD in Open Air

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Keywords: metal oxide nanostructures, PLD, open air, sensors, N_2O

Nitrous oxide (N_2O) emissions are a significant component of the anthropogenic influence on climate change and contribute to the greenhouse effect. Therefore, precise measuring/monitoring of N_2O is crucial for identifying environmental effects and reducing emissions.

In this work, nanostructures of well-known semiconductor metal oxides, such as ZnO, SnO_2, TiO_2, etc., were fabricated in view of possible application as a N_2O gas sensor. We produced samples by pulsed laser deposition (PLD) in air environment at atmospheric pressure (in open air). The PLD technology applied in air at atmospheric pressure leads to fabrication of highly porous nanoparticle structures. Such structures possess a high surface-to-volume ratio, which makes them suitable candidates for gas-sensor elements. We focused our attention on the morphology of the nanostructures produced by nanosecond (*ns*) and picosecond (*ps*) PLD from homemade ceramic targets (ZnO, SnO_2, TiO_2, and WO_3). It was found that *ns*-PLD in open air produces nanoparticles of uniform size, with the mean particle diameter varying in the range of 30-50 nm depending on the type of metal oxide. The morphology of the samples deposited by *ps*-PLD differs slightly from that of the samples produced by *ns*-PLD, mainly due to the appearance of a bi-modal particle size distribution typical for ultrashort laser ablation. The mean particle size for samples deposited by *ps* ablation reaches 50-90 nm. Further, similar experiments were carried out on PLD in open air from a pure Cu target to produce nanostructures composed of CuO nanoparticles. The PLD in open air technology allows us to fabricate composite structures consisting of n-type (ZnO, SnO_2, TiO_2, etc.) and p-type (CuO) metal-oxide nanoparticles. The formation of semiconductor heterojunctions is a prerequisite for improved gas sensor performance.

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Modified naphthalimides as frontrunners in the race for organic battery energy materials

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Keywords: Peri-annulated naphthalimides; bipolar organic materials; energy storage

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Organic electrode materials (OEMs) have attracted research interest in recent years because they combine environmental compatibility and high energy density with cost-effectiveness. The effectiveness of OEMs depends on their specific redox reactions, which can be divided into three categories based on their tendency to reduce or oxidize: *n*-, *p*-, and bipolar types.

This research reports peri-annulated naphthalimides (NIs) as bipolar organic materials for electrodes in rechargeable batteries [1,2]. The electrochemical properties were investigated in lithium-ion half-cells with an ionic liquid electrolyte. GCPL and cyclic voltammetry techniques are used to study the redox reactions in NIs. The cyclic stability of pristine organic matrices was compared to that of composites containing reduced graphene oxide. X-ray powder diffraction, scanning electron microscopy, and micro-Raman spectroscopy were used to analyze the structural, morphological, and compositional changes of the compounds before and after the electrochemical reaction.

Below 3.0 V vs. Li^+/Li, NIs interact with up to $4Li^+$ by the sequential reduction of the peri-dichalcogenide bridge and the carbonyl groups (*n*-type interaction). Beyond 4.0V vs. Li^+/Li, NIs undergo oxidation through the participation of the chalcogen atoms and carbonyl groups of the naphthalene moiety (*p*-type interaction).

Overall, the reported NIs have a bipolar molecular architecture that may be a starting point for further design of organic bipolar electrode materials.

Acknowledgements: The Bulgarian National Science Fund funded this study under grant number КП-06-H69/1 (8.12.2022). The electrochemical experiments were performed on equipment provided by the project BG05M2OP001-1.001-0008 "National Centre of Mechatronics and Clean Technologies", funded by the Operational Programme Science and Education for Smart Growth, co-financed by the European Union through the European Regional Development Fund. Part of the experiments were performed with equipment included in the National Infrastructure SI ESHER (NI SEVE) supported by the Bulgarian Ministry of Education and Science under grant agreement № Д01-349/13.12.2023.

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Bioactive composite and its impact on cancer cells

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Keywords: chitosan, Tanacetum parthenium, Feverfew, composites, anticancer

We focused on the synthesis of composites consisting of chitosan and herbal extract of Tanacetum parthenium (Feverfew). The composites of chitosan and Tanacetum parthenium were synthesized and characterized using techniques such as powder X-ray diffraction, infrared spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Their effectiveness was tested against various tumor cell.

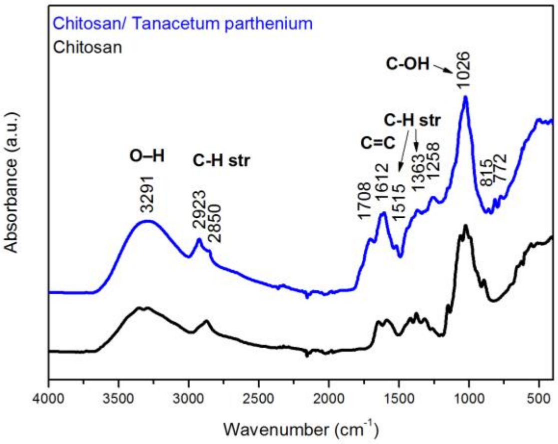

Figure 1. FTIR spectra of Chitosan and composite of Chitosa-Tanacetum perthenium.

The major observed peaks are more characteristic of phytocomponents including glycosides, terpenoids, flavonoids, and alkaloids that are present in the Tanacetum parthenium species. In MTT testing, a linear decrease in melanoma cells from the A375 line was observed, with increasing quantity. The Tanacetum parthenium extract placed on a chitosan carrier are a new solution for delivering active substances to cancer cells in order to eliminate them. Thus, the newly synthesized composites with Tanacetum parthenium extract represent a new opportunity for their use in the treatment of melanoma.

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Effect of Ni and rGO or NrGO additives on the hydriding/dehydriding properties of Mg

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Keywords: Mg- based materials, sorption kinetics, hydrogen storage, ball milling

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Hydrogen storage in metal hydrides especially in Mg-based one has some significant advantages, such as high gravimetric hydrogen storage capacity (7.6 wt. %), excellent reversibility and low coast. Nevertheless, these materials have slow reaction kinetics and high stability of hydrides. To improve their hydrogen storage properties ball milling and different additives to magnesium are used. The present study is focused on the hydrogen sorption characteristics of Mg with 5 wt. % Ni and 5 wt.% rGO or NrGO (reduced graphene oxide and Nitrogen doped reduced graphene oxide provided by Graphit Kropfmühl GmbH- Hauzenberg, Germany) prepared by ball milling in a planetary mill under argon atmosphere for 3 hours. The hydrogen sorption properties of the composites are studied at 473 and 573 K and a pressure of 1 MPa for absorption and 573 K and 623 K and 0.15 MPa for desorption using a volumetric Sievert's type apparatus. Structure, phase and surface composition of the starting compounds and the sample before and after hydriding are determined by XRD and TEM. The maximum achieved absorption capacity of the composite after 1h of hydriding at 573 K is 6.4 wt. % and 3 wt. % at 473 K for 90 wt.% Mg-5 wt.% Ni-5 wt.% NrGO and for 5.3 wt. % and 1.6 wt. % for 90 wt.% Mg-5 wt.% Ni-5 wt.% rGO. The desorption reaction is faster at 623 K and 0.15 MPa and after 1 h 6.2 wt.% H_2 is desorbed for the composite with NrGO and 4.7 for the other one with rGO. At lower temperature of 573 K the desorption properties are deteriorated significantly for both composites. The results from XRD and TEM characterizations after ten cycles of hydrogenation show mainly the presence of MgH_2 and Mg_2NiH_4 with monoclinic and orthorhombic structures, but also traces of MgO, unhydrided Mg and Ni. The presence of nickel and NrGO or rGO has a positive effect on hydrogenation kinetics and hydrogen storage capacity, but in the case of the combination of additives as Ni and NrGO the sorption kinetics is faster and the obtained capacity is higher. Moreover, the formation of ternary hydride Mg_2NiH_4 has also substantial role on the improvement of the hydrogen storage properties of magnesium.

Acknowledgements: Part of the experiments were performed with equipment included in the National Infrastructure SI ESHER (NI SEVE) supported by the Bulgarian Ministry of Education and Science under grant agreement № Д01-349/13.12.2023. The authors are sincerely grateful to Robert Feher from Graphit Kropfmühl GmbH (Hauzenberg, Germany) for providing rGO and NrGO additives.

Catalytic redox reaction pathways on chalcogenide complexes

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Keywords: carbonyls, nitrosyls, transition metal, sulfides, selenides

The transition metal chalcogenides (sulfides and selenides) of the 3d elements (Co, Fe, Ni, Cu) were examined by computational modelling as catalysts and photocatalysts in the following redox reactions: (i) CO_2 reduction, (ii) water splitting, (iii) NO reduction. The reaction mechanisms were studied by transition state theory. The transition metal complexes included a rhombic M_2X_2 core, where M=Fe, Co, Ni, Cu and X=S, Se. Different ligands were attached to the metal cations: chloride, carbonyl, and nitrosyl. The reactants, reaction intermediates and transition states were fully optimized using the B3LYP hybrid functional and gaussian basis sets. It was found, that all reactants and reaction intermediates absorb light in the visible range. The possibility of photoexcitation was assessed by TD-DFT. According to the results, cobalt and iron disulfide hexacarbonyl complexes provide the energetically most favorable pathway for redox reactions in CO_2 reduction and NO reduction and they also possess strong excitation bands in the visible region. With respect to water splitting, the cobalt and iron selenide complexes provide the lowest energy pathway.

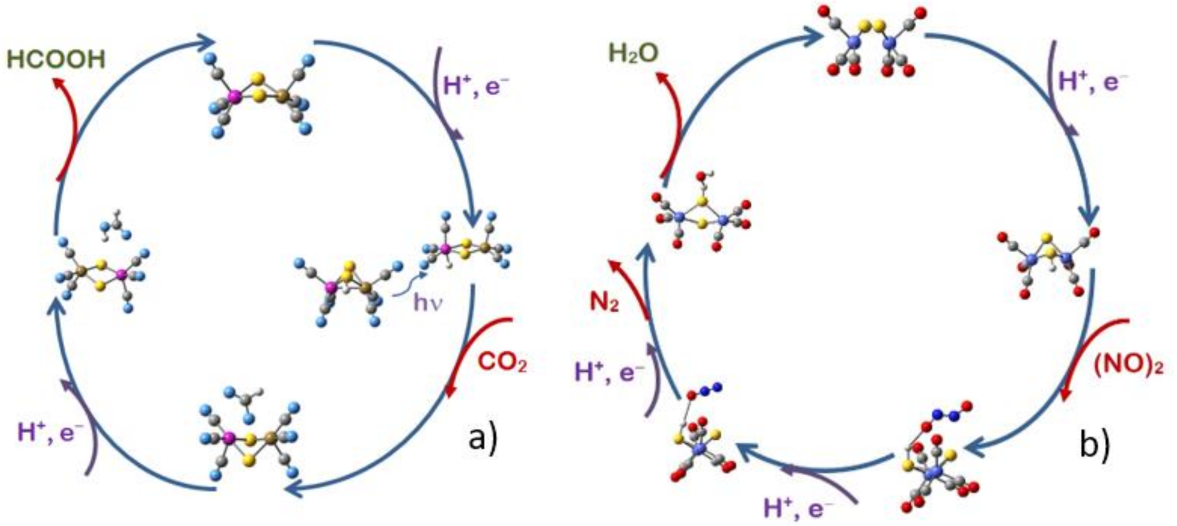

Figure 1. a) Pathway of photocatalytic CO_2 reduction to HCOOH on dimetal-disulfide hexacarbonyls. b) Pathway of NO reduction to N_2 via nitrosyl dimers $(NO)_2$.

Acknowledgements: The financial support from the Bulgarian National Science Fund of Bulgarian Ministry of Education and Science (MES), Grant КП-06-Н59/6 (2021), project (PhotoMetalMod)" is gratefully acknowledged, as well as the provided access to the e-infrastructure of the NCHDC - part of the Bulgarian National Roadmap on RIs, financially coordinated by the MES of the Republic of Bulgaria (Grant No D01-325/01.12.2023).

Study of the Synthesis of SiC by carbonization of (111) Si Substrates: The Role of Native Silicon Oxide by XPS

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Keywords: Silicon Carbide; Chemical Vapor Deposition; X-ray photoelectron spectroscopy

We report the results of a study of the synthesis of the so- called intermediate film of SiC by carbonization of {111} Si substrates at (1130- 1140)^{0}C as well as the influence of native oxide on the carbonization processes. The synthesis was carried out by the method of chemical vapor deposition with thermal decomposition of methane in hydrogen gas flow at (1130÷1140) °C. The experiments were carried out in an Oxford Nanofab Plasmalab System 100 apparatus. All experiments were performed both on substrates from which the native oxide was not removed and on substrates from which the native oxide was removed according to established protocols. The synthesis processes were carried out for 3, 5, 20, 60 and 90 min of carbon phase deposition time. The obtained thin films were analyzed by X- ray photoelectron spectroscopy. This technique as is well known could be used in non-destructive and destructive modes. For simple detection of surface concentrations of constituent element as well as the chemical bond among them in the deposited thin film we apply XPS in its nondestructive mode. Since our main focus is studying the synthesis of SiC on a Si (111) substrate by direct carbonization of the substrate, the distribution of elements in depth is very interesting. In our case we use depth resolution better than 3 nm and the information depth of a 45° exit angle measurement, which is around this size. All obtained result will be presented and discussed.

Acknowledgements: The authors gratefully acknowledge financial support by the National Science Fund of Bulgaria under grant KP-06-H58/2 – 16.11.2021

Advanced Carbon-Based Nanocomposites for Enhanced CO_2 Adsorption

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Keywords: nanocarbon, composites, reduced graphene oxide, carbon dots, CO_2 adsorption

Capturing CO_2 through adsorption onto solid materials presents a promising strategy, largely due to its low energy demands and straightforward implementation. This study focuses on developing effective CO_2 adsorbents based on composites of nanocarbon and reduced graphene oxide (RGO), synthesized using graphite, L-ascorbic acid (L-AA), and glycine as precursors.

The resulting materials were characterized using a suite of analytical techniques, including XRD, low-temperature nitrogen adsorption, FTIR, Raman, and XPS spectroscopies, as well as SEM and TEM imaging. Key adsorption parameters such as CO_2 uptake capacity, adsorption enthalpies, and selectivity were evaluated.

A hierarchical porous structure was observed in both the pure nanocarbons and their composites with RGO. Interestingly, the morphology of the nanocarbons and composites varied significantly depending on the precursor, which appeared to play a crucial role in the development of the porous architecture. Some materials displayed a unique textural synergy between nanocarbon and RGO components, resulting in novel structural properties.

The L-AA-derived samples contain spherical particles with average size of approx. 12 nm and core–shell morphology, suggesting the presence of carbon dots or dot-like particles. CO_2 adsorption measurements at 273 K and 100 kPa revealed that glycine-based materials owed their performance to nitrogen-containing functional groups, while the L-AA-derived composite benefited from the synergistic effect of carbon dots and RGO, which contributed to both effective oxygen surface functionalization and an optimized porous structure.

Adsorption heat measurements indicated chemisorption for both pure nanocarbons and the glycine-derived composite. Meanwhile, the L-AA-based composite demonstrated not only chemisorption but also sustained physisorption at higher CO_2 loadings.

The composite synthesized using L-ascorbic acid via a one-step, green, cost-efficient, and environmentally friendly method showed outstanding CO_2 adsorption performance. This is attributed to its well-balanced combination of oxygen-rich surface functionality and hierarchical porous structure, which also ensures high selectivity over nitrogen.

Acknowledgements: This research was funded by the National Science Fund, Project KP-06-H 59/8 "Porous 3D graphene-based hierarchical materials for environmental protection".
Research infrastructure support by the Ministry of Education and Science (project INFRAMAT) is acknowledged. Equipment by virtue of "Research, Innovation and Digitization for Smart Transformation" program 2021-2027 (Project BG16RFPR002-1.014-0006 "National Center of Excellence Mechatronics and Clean Technologies") supported by the European Regional Development Fund was also used.

Tautomerism and optical properties of 2-carbamido-1,3-indandione in solid state and solution. Experimental and theoretical study

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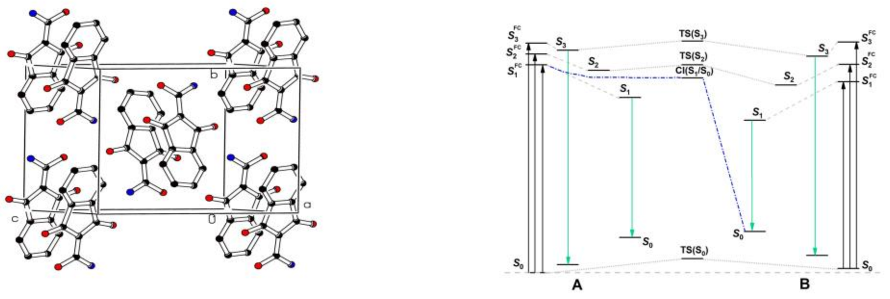
Keywords: 2-carbamido-1,3-indandione (CAID), proton transfer, UV-Vis, fluorescence, ab initio

2-Carbamido-1,3-indandione (CAID) is a fluorescent compound existing in two tautomeric forms: 2-(hydroxyl-aminomethylidene)-indan-1,3-dione (A) and 2-carboamide-1-hydroxy-3-oxo-indan (B), which are in a dynamic equilibrium and interconvert via intramolecular proton transfer. The observed spectroscopic features of CAID (IR, UV–Vis absorption and fluorescence) in solid state and various solutions suggest that the tautomeric equilibrium varies in the ground and excited state and depending on surroundings. The thermodynamic stability and population of the CAID tautomers, their photophysical properties and the energy barriers of tautomer conversion are evaluated in solution at molecular level using high *ab initio* level: SOS-MP2 and SOS-ADC(2) and in solid state by static and molecular dynamics calculations of the periodic structure. In the ground state, the tautomer A is of predominant amounts, while in all excited states the tautomer B is stabilized as a result of intramolecular proton transfer. A proposed combined theoretical and experimental approach revealed the excitation paths and phototautomerization in CAID and explained its photophysical processes. The unique optical properties, high photostability and low cytotoxicity of CAID make it a promising compound for practical applications as sunscreen and biosensor.



(a) (b)

Figure 1. (a) Solid state structure of CAID; (b) Photophysical and photochemical processes of CAID in ethanol. Tautomeric conversion A↔B through proton transfer in ground state S_0 and excited S_2 and S_3 states, and conical intersection S_1/S_0 are calculated at SOS-ADC(2)/def2-SVPD level of theory.

Acknowledgements: The authors thank for the financial support the Bulgarian National Science Fund of Bulgarian Ministry of Education and Science (MES), Grant КП-06-Н59/6 (2021), project “PhotoMetalMod”. The authors also acknowledge the provided access to the e-infrastructure of the NCHDC - part of the Bulgarian National Roadmap on RIs, financially coordinated by the MES of the Republic of Bulgaria (Grant No D01-325/01.12.2023).

Phyto-synthesized TiO_2 particles - antimicrobial activity against *E. coli*, *P. aeruginosa*, *B. subtilis* and *O. paurometabola*

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Keywords: green synthesis, TiO_2, physicochemical features, antimicrobial activity

The TiO_2 anatase nanoparticles were obtained by hydrothermal activation at two different temperatures of *Mentha Spicata* extract modified titanium solution. The prepared powders were characterized by: PXRD, FT-IR spectroscopy, SEM, EDS, TEM, XPS and BET analyses. The incorporation of the plant extract resulted in a slight decrease in the **c** lattice parameter of the phyto-nanoparticles, leading to a slight reduction in the unit cell volume. The degree of crystallinity increases with the hydrothermal temperature. It was established that the green samples possess higher specific surface area and better dispersion than those of the reference powders. The SEM revealed randomly oriented large irregular structures composed two types of aggregates: long type consists of dense matrix and the second type consists of smaller grains. The samples obtained at higher hydrothermal temperature possess the smallest particles sizes (8-12 nm). The synergistic effect of UV-light and particles on the bacterial strains was demonstrated. The phyto-synthesized powders showed a stronger inhibitory effect compared to that of the reference TiO_2. The synergistic antimicrobial effect of the particles and UV light was evident in all tested powders. The G- test bacteria exhibit greater sensitivity in comparison to that G+ bacteria. The high antibacterial activities are in correlation with the larger specific surface area and pore volume of green synthesized samples. The proposed by us plant-mediated synthesis is suitable for preparation of titania powders, having defined structure and morphological features, which lead to antimicrobial activities.

Acknowledgements: The authors express their gratitude to the project with the Bulgarian National Science Fund, KP-06-N69/8 (КП-06-Н69/8), "Novel polymer-hybrid materials containing (green)synthesized metal oxide particles with improved photocatalytic and antimicrobial potential" for the financial support.

Dysprosium doped glass-ceramics from the system Na_2O-Al_2O_3-SiO_2-B_2O_3 for LED

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Keywords: Silicate phosphor, Nano glass-ceramic, Rare-earth ions, X-ray, Photoluminescence

Dysprosium doped glasses from the system Na_2O-Al_2O_3-SiO_2-B_2O_3 with three different concentrations of the active ion - 0.5, 1 and 2 at. % are prepared after heating at 1300ºC during 3 hours. Glass-ceramics are obtained after thermal treatment of the parent glass at 580 and 630◦C during 2, 5 and 24 hours. The main crystallizing phases are $NaAlSiO_4$ in two different modifications and $Na_3B_3O_6$. The crystallinity degree and the nano crystalline size depend on the thermal treatment conditions and dopant concentration. XRD analyses show the presence of third unknown phase in some samples. Emission and excitation spectra of the glass-ceramics show the characteristic peaks of Dy^{3+} ($^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$ at 483 and 575 nm). The peak in yellow region is dominant, so the Dy^{3+} ion is located in the site without inversion center. The spectra show different intensity depending on the Dy^{3+} concentration and the thermal treatment conditions. This result suggests that the emission color can be controlled by these two factors. The lifetime measurements show that the Dy^{3+} ions occupy three different places in the glass-ceramic with different environment. The average lifetime also depends on the dopant concentration and the time treatment regime.

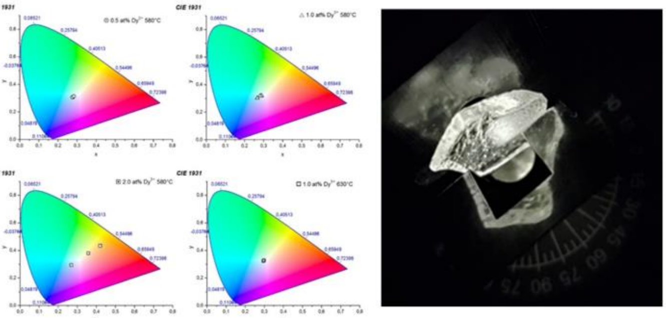

Figure 1. CIE coordinates of the glass-ceramic samples doped by 0.5, 1 and 2 at. % Dy^{3+} treated at 580 and 630◦C for 2, 5 and 24 hours and photograph of the glass-ceramic sample doped by 1 at. % Dy^{3+} treated at 580◦C for 2 hours.

Acknowledgements: This research is supported by the project BG05M2OP001-1.001-0008 "NATIONAL CENTER OF MECHATRONICS AND CLEAN TECHNOLOGIES **"**, funded by the Operational Programme Science and Education for Smart Growth 2014-2020, co-financed by the European Union through the European Regional Development Fund. Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by Bulgarian Ministry of Education and Science was used in this investigation.

Synthesis, Luminescent and Antibacterial Properties of Sol-Gel $TiO_2/TeO_2/Nb_2O_5$ Powders

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Keywords: sol-gel nanopowders; antibacterial properties

The present paper deals with the synthesis, characterization, and properties of sol-gel-derived $TiO_2/TeO_2/Nb_2O_5$ nanopowders. The gels were prepared using a combination of organic [Ti (IV) n-butoxide, Nb(V) ethoxide ($C_{10}H_{25}NbO_5$)] and inorganic [telluric acid (H_6TeO_6)] precursors. The aging of gels was performed in air for several days in order to enable further hydrolysis. The phase formation of the gels was investigated by XRD upon heating in the temperature range of 200–700°C. It was established that the gels heat-treated up to 300°C exhibited a predominantly amorphous phase in all binary and ternary compositions. The amount of amorphous phase gradually decreased with increasing temperature, and the first TiO_2 (anatase) crystals were detected at about 400–500°C. The average crystallite size of TiO_2 (anatase) in the powdered samples heat-treated at 400°C was about 10 nm. By DTA, it was established that the decomposition of organics is accompanied by strong weight loss occurring in the temperature range of 200–300°C. The completeness of the hydrolysis-condensation reactions was verified by IR and UV–Vis analyses. The UV–Vis spectra of the as-prepared gels exhibited red shifting of the cut-off. Photoluminescence spectra exhibited a change in intensity with varying temperature and composition. The performed photocatalytic tests showed that all powders possess photocatalytic activity toward Malachite green organic dye. The obtained nanopowders were tested for antimicrobial effect against *Pseuodomonas aeruginosa ATCC 27853, Staphylococcus aureus ATCC 25923* and *Candida albicans ATCC 18804*. The obtained samples can be considered as prospective materials for use as environmental catalysts.

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Synthesis, characterization, and activity of Pd-modified $SrWO_4$ catalyst for VOCs oxidation

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Keywords: Mechanochemical synthesis, $Pd/SrWO_4$, VOC oxidation

$SrWO_4$ nanoparticles were successfully obtained by direct mechanochemical synthesis at room temperature. To develop novel and efficient catalysts, $SrWO_4$ was modified with Pd and characterized with different instrumental techniques, such as: XRD, TEM and XPS. The results from the instrumental methods confirmed that $SrWO_4$ and $Pd/SrWO_4$ possess scheelite type of structure. XPS and TEM analyses reveal that palladium is homogeneously dispersed and it is present on the surface of $Pd/SrWO_4$ in different oxidation states. The catalytic properties of the obtained materials were investigated by the reactions of complete catalytic oxidation of methane, ethane, propane, butane, and ethylene (Figure 1).

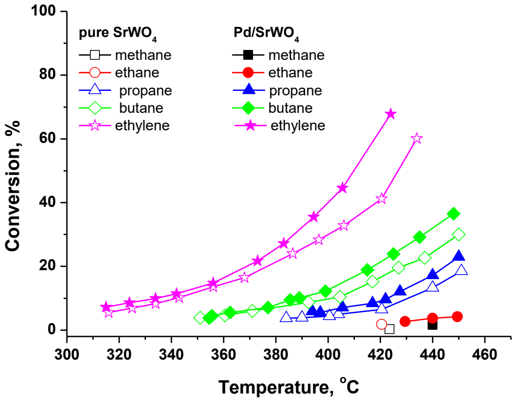

Figure 1. Dependencies of the conversion on the reaction temperature during complete oxidation of different hydrocarbons on pure $SrWO_4$ and Pd-modified $SrWO_4$.

The catalytic test shows the lowest value for T_{50} was observed for the combustion of ethylene. On the base of the obtained results, one may conclude that the $Pd/SrWO_4$ can be considered as perspective material for use as an active phase in the preparation of environmental catalysts.

Acknowledgements: The Thermo FID-TG analyzer under the project No. BG16RFPR002-1.014-0006 “National Center of Excellence Mechatronics and Clean Technologies “supported by the European Regional Development Fund under “Research Innovation and Digitization for Smart Transformation” program 2021–2027, was used for the experimental work.

Catalytic Combustion of Volatile Organic Compounds over La-Sr-Fe Perovskite-related Catalysts

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Keywords: La-Sr-Fe Perovskite-related Catalysts, VOC oxidation, Reaction kinetics, Mechanism

A La-Sr-Fe perovskite-related catalysts with nominal compositions $La_{1-x}Sr_xFeO_4$, where $x = 0.5$, 1, and 1.5 was synthesized and evaluated for its performance in the catalytic oxidation of volatile organic compounds (VOCs). The catalyst was prepared using a sol-gel auto-combustion technique and thoroughly characterized by techniques including N_2-physisorption, X-ray diffraction, Mössbauer spectroscopy, X-ray photoelectron spectroscopy, Temperature programmed reduction, and Temperature programmed desorption.

The catalysts were tested in complete oxidation of the following VOCs: methane, ethane, ethylene, propane, and butane. The selected organic compounds represent C_1-C_4 hydrocarbons are of potential interest due to their high global warming potential (GWP). It was observed that, depending on the VOCs, the reaction proceeds at temperatures above 200 °C. Ethane and ethylene were additionally investigated aiming to obtain data on the kinetics and to shed some light on the reaction mechanism. The obtained results show partial reaction order towards the VOCs, ranging at values of 0.8, revealing a weak adsorption on the catalytic surface. In contrast, the reaction order towards the oxygen has values around 0.1, thus showing a very strong, most probably dissociative adsorption of oxygen on the surface. Based on the results from the power-law kinetics study and the data from the TPD and TPR, a set of probable reaction mechanism has been proposed. The work continues on the mechanistic analysis of the obtained results, aiming to suggest the most probable mechanism of the reactions.

Acknowledgments: This work was supported by the Bulgarian Science Fund (Contract No. КП-06-Н89/5).

Kinetic Studies on the Interaction Between Dentine-Like Hydroxyapatite and Hydroxyapatite Ceramic with Dental Functional Monomer 4-META

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Keywords: 4-Methacryloxyethyl trimellitic anhydride; Hydroxyapatite; Solid state NMR; Kinetics

Secondary caries is a serious problem in surgical disease. To reduce its risk, adhesive bonding systems containing functional monomers such as dipentaerythritol pentaacrylate phosphoric acid ester (PENTA), 4-methacryloxyethyl trimellitate (4-MET) or its anhydride form (4-META), methacryloyloxydecyl dihydrogen phosphate (10-MDP), etc., are used. They strongly bond the natural hard tissue (enamel/dentin) and the restorative material (filling/crown).

In this study, we synthesised dentine-like hydroxyapatite (HA65) as a representative of natural dentin and hydroxyapatite ceramic powder (HA1000) as a representative of recovery material. Further, we followed the changes in solid and liquid phases during their interaction with the water-ethanolic solution of the monomer 4-methacryloxyethyl trimellitic anhydride (4-META), as one of the most promising reactive monomers.

The results of kinetic studies showed that at the same immersion time in the freshly prepared solution of 4-META, the adsorption of the latter was higher by dentin-like HA (HA65) than by HA ceramic (HA1000) due to its higher specific surface area and smaller particle size. In both cases, the appearance of acid calcium phosphate (dicalcium phosphate dihydrate) over time was identified. Furthermore, NMR studies showed that the higher adsorption of 4-META by HA65 effectively prevents the hydrolysis and degradation of 4-META in solution, while in the presence of HA1000 4-META undergoes changes under the experimental conditions related to the hydrolysis and partial polymerization processes.

We investigated the stability of the obtained HA65-4-META derivative, as a representative of 4-META-treated dentin surfaces, in acidic solutions and compared it with that of pure dentin-like HA. The total Ca concentration upon dissolution of HA65-4-META in a 0.1 mol/L lactic acid solution is three times lower than the total Ca concentration upon dissolution of pure HA65. This, as well as the established presence of 4-META and its hydrolysis derivatives in the HA65-4-META after 14 days of immersion indicates that the 4-META-treated dentin-like surfaces are more resistant to dissolution in an acidic environment than the untreated ones, which results in protection of the treated tooth surface from the formation of secondary caries.

FTIR Spectroscopy of $^{15}N_2$ Adsorption on Shape-Controlled Ceria Nanocrystals

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Keywords: Adsorption, dinitrogen, FTIR spectroscopy, ceria, probe molecules

Due to the easy switching between Ce^{4+} and Ce^{3+}, ceria and related materials are widely used in redox catalysis. Additionally, their performance strongly depends on crystal morphology. FTIR spectroscopy with probe molecules can provide valuable insights into their surface properties. Although CO is the most commonly used probe, N_2 offers key advantages: it does not reduce Ce^{4+}, does not form surface anionic species, and is infrared-transparent in the gaseous state.

Because N_2 adsorption is weak, measurements are performed at liquid nitrogen temperatures. To avoid spectroscopic interference from atmospheric CO_2, the $^{15}N_2$ isotopologue is used.

Stoichiometric ceria nanocrystallites with different shapes (cubes, rods, and polyhedra) and preferentially exposed low-index planes have been studied. Using $^{15}N_2$ as a probe, we demonstrated that it can distinguish between Ce^{4+} sites on {110} facets and edges (band at 2257 cm^{-1}) and those on {100} (2252 cm^{-1}). The {111} facets are inert.

After reduction of the ceria samples with hydrogen, the two bands of adsorbed $^{15}N_2$ merge into a single band at an intermediate position (2256 cm^{-1}) with a weak shoulder at 2254 cm^{-1}. These bands are attributed to $^{15}N_2$ species adsorbed on Ce^{3+} sites from the {100} and eventually {111} facets of the crystallites, while the {111} facets are again inert. Notably, $^{15}N_2$ adsorption also induces a red shift of some components of the band due to Ce^{3+} electronic transitions.

Conclusion: FTIR of adsorbed $^{15}N_2$ can detect and distinguish only Ce^{4+} sites on the more reactive low-index planes such as {110} and {100}, which may be an advantage for characterizing ceria samples. Despite spectral overlap, $^{15}N_2$ complexes with Ce^{4+} and Ce^{3+} may also be spectroscopically distinguishable.

Acknowledgements: This work was supported by the Bulgarian Science Fund (Program VIHREN, Project number КП-06-ДВ-1).

Analysis of multicomponent solutions, used in adsorption experiments with spent coffee grounds, by means of TXRF spectrometry

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Keywords: coffee grounds, adsorption, TXRF analysis

Water pollution by toxic metals is a serious and worldwide environmental problem nowadays. The use of cheap and abundant biomaterials can help solve this problem. Spent coffee grounds is a waste biomaterial, available in huge amounts, that can remove heavy metals from contaminated water. In this study, this biomass is examined for its capacity to simultaneously remove pollutants as Cu, Zn and Cd from water. Initial concentration 100 mg L^{-1} (for each ion) and pH 4 were used in batch experiments to investigate the effect of contact time on metal ion adsorption.

The simultaneous determination of the three pollutant elements in the solution, both before and after the adsorption process, was performed using total reflection X-ray fluorescence (TXRF) spectrometry. The measurements were carried out under optimized experimental conditions. Gallium was used as an internal standard at concentrations of 1 mg L^{-1} and 10 mg L^{-1}. Aliquots of 5 µL were pipetted onto acrylic disks and dried under an infrared lamp, ensuring a thin and uniform layer for analysis. The concentrations of Cu and Zn were determined by excitation of their $K\alpha_{1,2}$ fluorescence lines, while for Cd, only the less sensitive $L\alpha_1$ line could be used. An exposure time of 100 s was sufficient for the quantification of the analyzed elements. The results showed good agreement with those obtained using conventional flame atomic absorption spectrometry (AAS).

The findings of this study demonstrated that the optimized TXRF procedureis is suitable for analysis of multicomponent solutions, used in adsorption experiments with spent coffee grounds. The kinetic investigation confirmed the potential of this biomass as an effective biosorbent for water purification.

Acknowledgements: The authors acknowledge the financial support for the TXRF equipment used in this investigation by European Regional Development Fund under "Research Innovation and Digitization for Smart Transformation" program 2021-2027 under the Project "National Center of Excellence Mechatronics and Clean Technologies"; National Scientific Infrastructure "Energy Storage and Hydrogen Energy" (ESHER), funded by the Ministry of Education and Science, contract No. DO1-349/13.12.2023; distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science.

A Database for Energy-Storage Materials and Time Series Machine Learning Models for Organic Electrode Materials

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Keywords: dataset, organic energy-storage materials, time series machine learning

In the last decade, the data-driven methods for materials discovery gained significant popularity since they are capable of recognizing complex nonlinear relationships in large sets of experimental or theoretically derived data. The existence of well-curated datasets is crucial for the successful application of such methods. Since a limited number of open-access datasets for redox-materials is available [1], the present study aims to establish a scheme of a relational database that is capable to efficiently manage the input, storage, and retrievement of experimental data related to electrode materials.

Redox-active organic compounds, on the other hand are promising cathode materials due to their high energy density per unit of mass, structure tunability (organic materials can be synthetically modified to attain a desired property such as high potential or low solubility in the electrolyte solvent), low toxicity and environmental compatibility.

To test the database scheme developed, the characterization (spectral and electrochemical) data of a set of peri-annulated naphthalimide electrode materials [2] is recorded to the database and different time-series machine learning algorithms are used to predict the onset of degradation processes.

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Glass-Ceramic Materials with Luminescent Properties in the system ZnO-B_2O_3-Nb_2O_5-Eu_2O_3

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Keywords: glass ceramics; XRD; TEM; luminescence

The crystallization behavior of $50ZnO:47B_2O_3:3Nb_2O_3:0.5Eu_2O_3$ glass has been investigated i by DSC, XRD and TEM analysis. The luminescent properties of the resulting glass-ceramics were investigated. By XRD and TEM analysis, crystallization of several crystalline phases has been proved (α-$Zn_3B_2O_6$, β-$Zn_3B_2O_6$ and $ZnNb_2O_6$). By calculating crystal parameters, it was found that europium ions are successfully incorporated in the β-$Zn_3B_2O_6$. Photoluminescence spectra showed increased emission in the resulting glass-ceramic samples compared to the parent glass sample due to higher asymmetry of Eu3+ ions in the obtained crystalline phases (Figure 1). It was established that the optimum emission intensity is registered for glass-ceramic samples obtained after 25 h heat treatment of the parent glass.

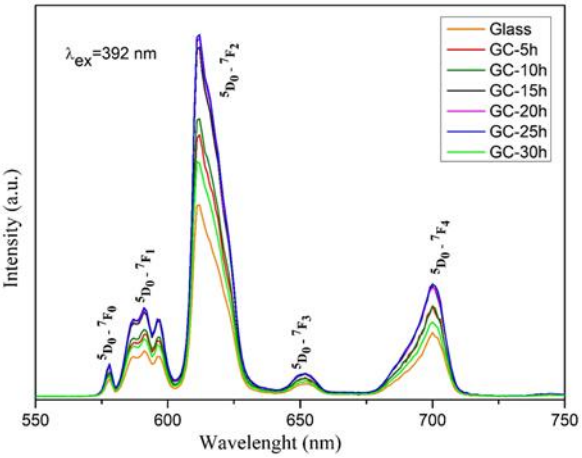

Figure 1. Emission spectra of 50ZnO:47B2O3:3Nb2O5:0.5Eu2O3 glass and the corresponding glass-ceramics heat treated over different time durations.

Acknowledgements: Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by the Bulgarian Ministry of Education and Science.

Synthesis and structure of Dy^{3+} doped and Dy^{3+}/Eu^{3+} co-doped $50ZnO.40B_2O_3.5WO_3.5Nb_2O_5$ glass

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Keywords: glasses; rare earths; density; Raman

In this study we have reported for the preparation and structure of Dy^{3+} and Eu^{3+} single doped, and Dy^{3+}/Eu^{3+} co-doped $ZnO\text{-}B_2O_3\text{-}WO_3\text{-}Nb_2O_5$ glasses. The materials were successfully synthesized by melt quenching method. The amorphous character of the prepared samples was confirmed by the X-ray diffraction(XRD). By Differential Scanning Calorimetry (DSC) it was found that the glass transition temperature, T_g for all glasses is over 500°C, while the crystallization temperature, T_c, varies between 695–730°C. All glasses are characterized with a high thermal stability i.e., $\Delta T = T_c - T_g$ between 178 and 210°C.

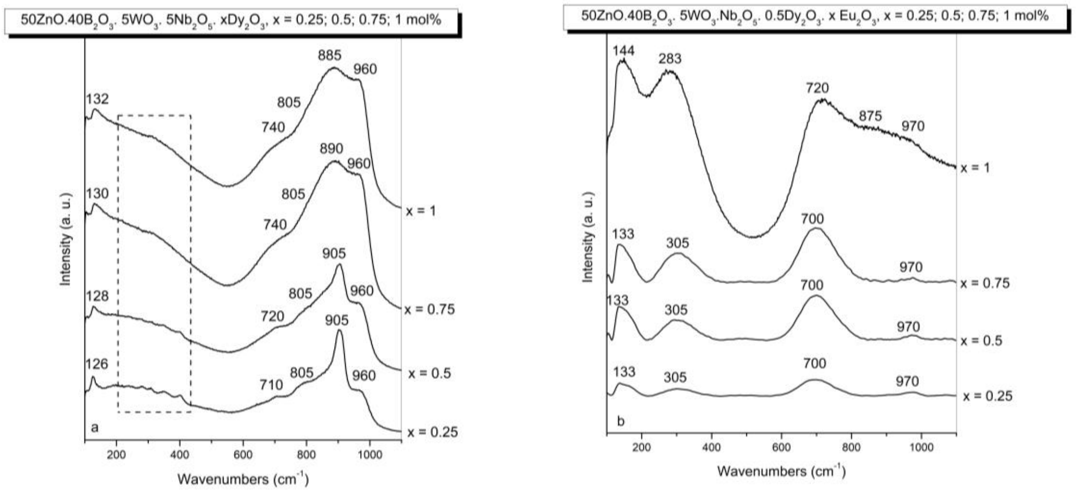

Figure 1. Raman spectra of the investigated glasses: a) Dy^{3+} doped $50ZnO:40B_2O_3:5WO_3:5Nb_2O_5$ glasses b) Dy^{3+}/Eu^{3+} co-doped $50ZnO:40B_2O_3:5WO_3:5Nb_2O_5$ glasses

Raman analysis revealed that the glass network consists of $[WO_4]^{2-}$ and $[NbO_4]^{3-}$ tetrahedral units, NbO_6 octahedra and metaborate units, $[BØ_2O]^-$. Physical properties like density, molar volume, oxygen molar volume and oxygen packing density of the glasses were also determined. The physical parameters evidenced a highly cross linked and connected network of the host glass $50ZnO.40B_2O_3 .5WO_3 .5Nb_2O_5$, that is very suitable for incorporating the rare earth active ions.

Acknowledgements: Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by the Bulgarian Ministry of Education and Science.

Structural and optical properties of $BaWO_4$ obtained by fast mechanochemical treatment

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Keywords: ball milling, nanoparticles, blue emission

This work investigated the optical characteristics of BaWO4 nanoparticles produced through direct mechanochemical synthesis at varying milling speeds. A stoichiometric mixture of $BaCO_3$ and WO_3 in a molar ratio of 1 : 1 was subjected to intense mechanical treatment in air using a planetary ball mill by applying two milling speeds: 500 and 850 rpm. The final products were characterizated by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), Raman, infrared (IR) and photoluminescence (PL) spectroscopies. The crystalitte and particles size was established by X-ray diffraction and SEM analysis. The particles with round shape and size bellow 50 nm was formed at different milling conditions. The Raman spectra of the synthesized samples confirm the presence of a scheelite type structure characterized by six distinct vibrational peaks. The symmetry of the main structural WO_4 groups is determined by IR spectroscopy. The strong (400nm) and weak (465 nm) emission peaks was observed for $BaWO_4$ obtained at higher milling speed, while wider emission at 410 is visible for $BaWO_4$ prepared at lower milling speed. The CIE coordinates of the mechanochemically synthesized $BaWO_4$ are located within the blue area, exhibiting various positions.

Acknowledgements: Research equipment of distributed research infrastructure INFRAMAT (part of Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science under contract D01-322/30.11.2023 were used in this investigation. The Raman equipment and investigation were supported by the European Regional Development Fund under the “Research Innovation and Digitization for Smart Transformation” program 2021–2027 under the Project BG16RFPR002-1.014-0006 “National Center of Excellence Mechatronics and Clean Technologies”.

Revealing the features facilitating the reversible insertion of sodium into hard carbons

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Keywords: hard carbon, bio-waste derived carnons, sodium-ion insertionsustainable energy storage

Searching for high-performance, low-cost and sustainable electrode materials for sodium-ion batteries, bio-hard carbonaceous materials (bio-HCs) appear as an absolute favorite. The main drawbacks of bio-HCs are their critical dependence on the choice of the biomass precursors and the synthesis procedure. Therefore, the state-of-the-art research is directed to understand the relationships between synthetic conditions and electrochemical properties of bio-HCs.

Herein, we compare the Na-storage properties of biowaste-derived hard caprbons (bio-HCs) from spent coffee grounds (SCGs) and walnut shell waste (WS). The SCGs-derived carbons were prepared by a torrefaction at relatively low temperature (750 ^{o}C) and subsequent high temperature pyrolysis at 1300 °C, while pyrolysis and hydropyrolysis techniqniques were applied for the synthesis of WS-derived carbons. In order to evaluate the influence of the mineral content of the raw material, part of the solid residue from torrefaction of SCGs was chemically treated until complete ash removal [1]. Another approach allowing to trace the influence of the main building components of biomass is preliminary acid treatment of the raw material. For this purpose, the walnut shells are soaked for a certain time in acid to eliminate hemicelluloses and part of the cellulose. The effect of the synthesis procedure on the carbon micrstructure and porosity were examined [1]. The electrochemical properties of bio-HCs were analysed in model Na-ion cells with carbonate-based sodium electrolyte [1,2]. To quantify the Na-storage performance of bio-HCs, we determined four parameters: reversible specific capacity, first irreversible capacity, cycling stability and rate capability [1,2]. In general, the presence of mineral ash and its distribution on the carbon surface helps to improve the performance of SCG-derived carbons [1]. Furthermore, it is established that WS -derived carbons outperforms SCGs –analogues, as the best electrochemical performance shows acid pretreated WS -derived carbon. Based on its excellent electrochemical performance, these HCs was used as negative electrodes in full sodium-ion cells with sodium transition-metal oxides as positive electrodes. The full-cells testing demonstrates that biowaste-derived hard carbons are a valuable material with potential applications for energy storage in sodium-ion batteries.

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Optimization of the magnetron sputtering process for the synthesis of thin films of ZnO and TiO_2 with gas sensitive properties

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Keywords: Magnetron sputtering, gas sensors, ZnO, TiO_2

The technology of magnetron sputtering plays an essential role in the development of gas sensors by enabling the synthesis of thin films with stable and reproducible gas-sensitive characteristics. Gas sensors are widely used in industry, environmental monitoring, and medicine for the detection and measurement of various gases. Among the most promising materials for sensor applications are ZnO and TiO_2, distinguished by their chemical stability, gas sensitivity, and suitable electrical properties.

In the present study, thin mixed oxide layers were developed through simultaneous magnetron sputtering of Zn and Ti in an argon and oxygen atmosphere. Zn was sputtered using a radio frequency RF source (100 W), while Ti was sputtered using a direct current DC source at powers ranging from 10 to 40 W. The aim was to optimize the Zn:Ti ratio in order to achieve improved gas sensitivity. X-ray photoelectron spectroscopy analysis, chosen due to the surface nature of gas reactions, showed that Zn is in a 2^+ valence state, while Ti exhibits several oxidation states. The formation of oxygen vacancies resulting from the lower oxidation states of titanium enhances the sensitivity of the layers to reducing gases by accelerating the adsorption and reaction of gas molecules.

The combined application of ZnO and TiO_2 in thin films obtained by magnetron sputtering is a promising approach for the development of highly sensitive and stable gas sensors.

Acknowledgements: The authors are grateful to the project KP-06-N87/8 " Development of sensor elements based on composite metal-oxide thin films and nanostructures", funded by the National Science Fund, Bulgaria, for the financial support to realize these investigations.

FTIR Spectroscopy Study of the Interaction between CO_2 and H_2 over Ni/ZSM-5 Catalysts

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Keywords: Adsorption, catalysis, FTIR spectroscopy, Ni/ZSM-5, probe molecules

CO_2 capture from waste gases is a critical and timely challenge in the context of climate change. Combining CO_2 capture with its utilization represents a highly attractive strategy. In this regard, nickel-containing zeolites appear particularly promising for two main reasons: (i) zeolites exhibit high CO_2 adsorption capacity, and (ii) supported nickel catalysts are active in various CO_2 conversion reactions. This work presents a pilot study on the interaction between CO_2 and hydrogen over two nickel-containing ZSM-5 samples (NiZ1 and NiZ2), which differ in their preparation methods - conventional ion exchange and solid-phase exchange, respectively. The investigation was conducted using in situ IR spectroscopy.

Adsorption of CO_2 on both samples leads to the formation of CO_2 species coordinated through one oxygen atom to nickel cations and hydroxyl groups, as indicated by IR bands at 2355–2346 cm^{-1} and 1375 cm^{-1}.

Upon heating the catalysts in a $CO_2 + H_2$ gas mixture at 100–275 °C (in steps of 25°C), several surface species and gas-phase products were detected:

- Adsorbed water (1620 cm^{-1}): Formed in significant amounts even at 100 °C, with intensity increasing at higher temperatures.
- Surface formates (1587 and 1380 cm^{-1}): Observed at 100 °C and developing up to 200 °C, after which they begin to decompose.
- Carbon monoxide: Adsorbed CO appears above 175 °C in the form of Ni^+–CO (2109 cm^{-1}) and $Ni^+(CO)_2$ (2137 and 2092 cm^{-1}). These species confirm partial reduction of Ni^{2+} to Ni^+. Gas-phase CO is detected above 225 °C.
- Methane: Detected only in the gas phase (3016 cm^{-1}) above 225 °C, primarily for the NiZ2 sample.

Conclusion: The results demonstrate that CO_2 can react with H_2 at relatively low temperatures and that the reaction pathways depend on the catalyst composition. These results suggest promising directions for optimizing the nickel content and preparation method to enhance CO_2 conversion under mild conditions.

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Ni–Mn oxide catalysts: From synthesis to application in VOCs oxidation

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Keywords: Catalyst preparation, Catalytic activity, Ni - modified MnO_x, VOCs oxidation

Volatile organic compounds (VOCs) represent a major class of air pollutants due to their detrimental impact on both environmental quality and human health. Among various strategies for mitigation of low-concentration industrial gas emissions, catalytic oxidation has proven to be one of the most efficient and reliable methods. While noble metals such as Pt, Pd, and Ru are traditionally employed as active components in VOC abatement catalysts, their widespread application is limited by high costs and insufficient thermal stability. In this context, transition metal oxides have emerged increasing attention as promising alternatives, offering comparable or even superior catalytic performance at a significantly lower cost.

In the present study, Ni-modified manganese oxides (MnOx) were synthesized via a co-precipitation method using various precursor compounds. The resulting materials were characterized using a range of analytical techniques. XRD analysis confirmed the formation of oxide phases, as well as the emergence of $NiMnO_3$ with an ilmenite-type crystal structure. The catalytic activity of these Ni-modified MnOx materials was evaluated through complete oxidation reactions of methane, ethane, propane, and butane. For practical implementation, a catalyst synthesized from nitrate precursors was supported on a ceramic substrate and tested for propane combustion as a model reaction.

Based on the experimental findings, $NiMnO_3$ with an ilmenite structure demonstrates strong potential as an active component for the development of cost-effective and efficient environmental catalysts.

Acknowledgements: The Thermo FID-TG analyzer and MultiGas FTIR Gas Analyzer 2030G under the project No. BG16RFPR002-1.014-0006 "National Center of Excellence Mechatronics and Clean Technologies" supported by the European Regional Development Fund under "Research Innovation and Digitization for Smart Transformation" program 2021–2027, was used for the experimental work.

Challenges in TEM characterization of magnesium-based sensitive materials

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Keywords: Mg-based materials, hydrogen storage, TEM characterization

Transmission electron microscopy (TEM) characterization of hydrogen storage materials based on Mg is somehow challenging because of their sensitivity to oxidation and the high energy of the electron beam exposure in TEM, which could cause negative impact. Some ways that minimize the damage of the samples are using more intense electron sources with more sensitive electron detectors, digital control of the beam in STEMs, using low noise, charge-coupled device (CCD) cameras and specimen cooling (cryo-microscopy) or combination of some of them. The nanoporous carbons prepared by hydropyrolysis from different precursors cherry stones and crushed walnut shell and from polyolefin wax ball milled under Ar and after hydrogenation at 300^0C and 1 MPa with composition 80 wt % MgH_2 - 15 wt% Ni- 5 wt % nanoporous carbons are analyzed by TEM (TEM HR STEM JEOL JEM 2100 with GATAN Orius 832 SC1000 CCD Camera). Structure, phase and surface composition of obtained materials are examined by TEM at accelerating voltage of 200 kV. By HRTEM is obtained information that the nanoporous carbons contain mainly graphitic structure, but also some phases like oxides, carbonates and hydroxides of calcium and magnesium from the biomass precursors (Fig.1).

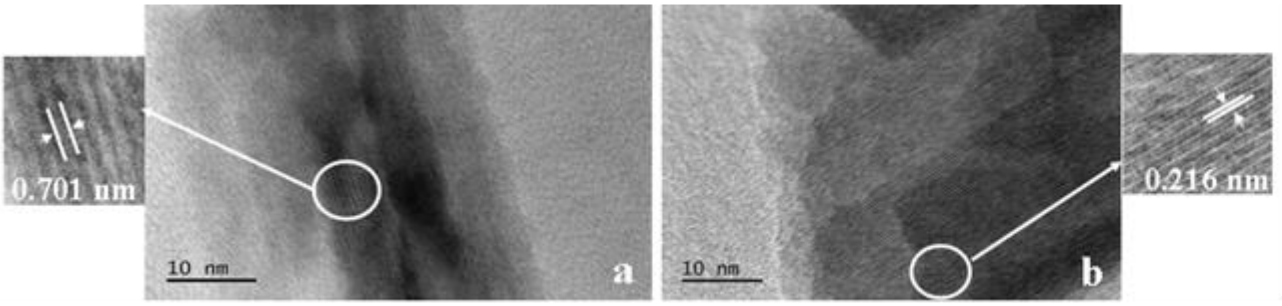

Figure 1. Experimental HRTEM pictures and Fourier filtered images of nanoporous carbons from: a) from cherry stones and b) crushed walnut shell.

The SAED and HRTEM observation revealed that the samples after hydrogenation at 300^0 C and a pressure of 1 MPa consists of MgH_2, but also orthorhombic Mg_2NiH_4 and the same ternary hydride with orthorhombic structure.

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TEM investigation of silver nanoparticles

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Keywords: TEM, silver nano particles, size distribution

Ag nanoparticles in a SiO_2 matrix were prepared using the sol-gel method. The precursors consisted of tetraethyl orthosilicate (TEOS), silver nitrate ($AgNO_3$), ethanol, nitric acid (HNO_3), and distilled water. The molar ratio of TEOS: C_2H_5OH: HNO_3: H_2O was 1:4:0.15:10, respectively.

In the first step, $AgNO_3$ and distilled water were mixed and stirred for 30 minutes at room temperature. In a separate beaker, TEOS and ethanol were also mixed and stirred for 30 minutes. The two solutions were then combined and homogenized under continuous stirring. After an additional 30 minutes of stirring, HNO_3, ethanol, and distilled water were added to the mixture. The final solution was continuously stirred for 4 hours at room temperature.

The morphology of the synthesized nanosized materials was investigated using transmission electron microscopy (TEM). Bright-field images of the sample were obtained at various magnifications. Particle size distribution was determined using the image processing software ImageJ. The average particle size of the sample was approximately 25 nm, with most nanoparticles ranging from 10 to 30 nm in size.

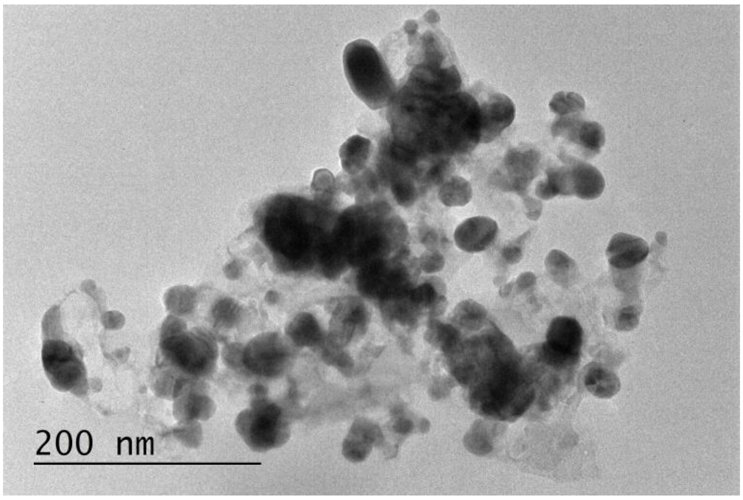

Figure 1. Bright field micrograph of silver nano particles at magnification 40 000

Utilization of Biomass Waste as a Low-Cost Adsorbent for Dye Removal

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Keywords: Black cumin seed waste; Toluidine blue, Adsorption

Residual synthetic dyes in industrial wastewater pose significant environmental and health hazards due to their toxic, stable, and non-biodegradable nature. Toluidine Blue, commonly used in medical and industrial fields, is particularly harmful and potentially carcinogenic. It disrupts aquatic ecosystems by reducing sunlight penetration and photosynthesis, and may contaminate drinking water. Effective removal of Toluidine Blue from wastewater is crucial for protecting public health and the environment. Low-cost adsorbents, often derived from agricultural or industrial waste, are popular in treatment processes due to their availability and low processing requirements. This study explores waste from black cumin seeds after oil extraction as an affordable and efficient biosorbent for dye removal.

The properties of the biomaterial were characterized using FTIR, SEM, and N_2 adsorption/desorption isotherm. Adsorption performance was evaluated under varying conditions, including dye concentration, contact time, temperature, and pH. The process followed the pseudo-second-order kinetic model and fit well with the Langmuir isotherm, indicating monolayer adsorption on a homogeneous surface. Thermodynamic parameters (negative ΔH^0 and ΔG^0, positive ΔS^0) confirmed that the adsorption of Toluidine Blue (TB) was spontaneous, exothermic, and entropy-driven. Physical interactions such as electrostatic attraction, van der Waals forces, and hydrogen bonding played a key role in TB removal. The adsorption was highly efficient and only minimally influenced by pH. A maximum adsorption capacity of 305 mg/g was recorded at 20°C, surpassing many other low-cost adsorbents. The natural porosity and surface chemistry of Black Cumin Seed Oil Press Cake enhance its dye-capturing ability, while its high desorption efficiency supports the predominance of physical adsorption and suggests potential for reuse. These results underscore its value as a sustainable and cost-effective biosorbent for wastewater treatment.

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Advanced Graphene Material for the Purification of Dye-Contaminated Water

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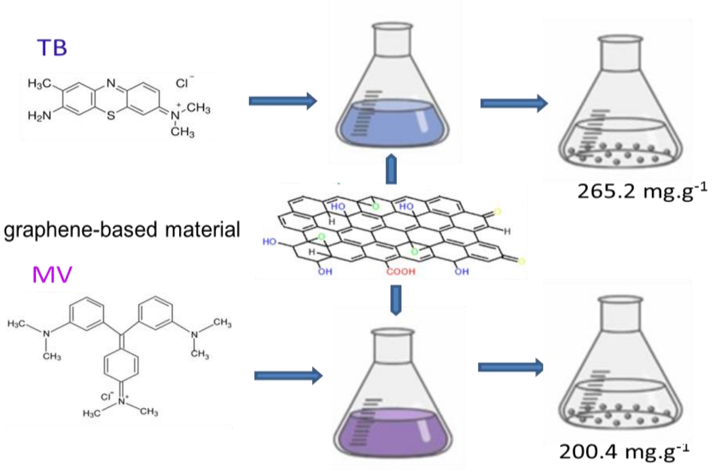
Keywords: graphene; toluidine blue; methyl violet; adsorption; dye removal

Access to safe and clean drinking water is crucial for the health and survival of all living organisms. Industrial effluents, particularly from textile and dyeing industries, are major contributors to water pollution, releasing large amounts of synthetic dyes into aquatic environments. These dyes are often toxic, persistent, and difficult to degrade, making their removal a pressing environmental challenge. In this work, a graphene-based adsorbent with high surface area and pore volume was synthesized using a modified, environmentally friendly method. The material was tested for its efficiency in removing cationic dyes - toluidine blue(TB) and methyl violet (MV) from aqueous solutions.



Characterization through XRD, TG-DTA, FTIR, and XPS confirmed partial reduction of graphene oxide to reduced graphene oxide through freeze-drying. Adsorption experiments examined the effects of pH, contact time, dye concentration, and temperature. The process followed pseudo-second-order kinetics and fitted well with the Langmuir isotherm model. Thermodynamic analysis revealed that the adsorption of both dyes was spontaneous and exothermic., accompanied by a decrease in entropy. The adsorbent exhibited impressive adsorption capacities for TB and MV, outperforming many reported materials. Adsorption was mainly driven by physical interactions, including electrostatic attraction, hydrogen bonding, and π-π stacking. These results underscore the potential of the synthesized graphene-based material as an efficient adsorbent for dye removal and point to future opportunities for enhancing its performance through targeted surface functionalization strategies.

Acknowledgements: The authors are thankful to Project KP-06-H 59/8 "Porous 3D graphene-based hierarchical materials for environmental protection" for the financial support". Equipment by virtue of "Research Innovation and Digitization for Smart Transformation" program 2021-2027 (Project BG16RFPR002-1.014-0006 "National Center of Excellence Mechatronics and Clean Technologies") supported by the European Regional Development Fund was used.

Catalytic Oxidation of Methane over a Pd-supported La_2O_3-CeO_2-ZrO_2-Al_2O_3 Mixed Oxide Catalyst

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Keywords: Pd catalyst, La_2O_3-CeO_2-ZrO_2-Al_2O_3 oxide support; methane combustion

This study invesigate a palladium-modified La_2O_3–CeO_2–ZrO_2–Al_2O_3 catalyst synthesized via the sol–gel method, focusing on its potential application in methane abatement. The catalyst was characterized using low-temperature N_2 adsorption, XRD, TEM, XPS, TPD and TPR. Palladium deposited on the supports results in the formation of palladium oxide. Following the catalytic experiments, the presence of metallic palladium is detected. Complete methane oxidation over the Pd/La_2O_3-CeO_2-ZrO_2-Al_2O_3 catalyst is achieved at temperatures above 250°C. However, under humid conditions, the required temperature for complete conversion increases by approximately 70 °C. Incorporating ZrO_2 into the support composition promotes the formation of a mixed oxide phase capable of interacting with palladium ions through reversible incorporation and release under varying conditions. The catalytic oxidation is believed to proceed predominantly via the Mars–van Krevelen mechanism. The study also assesses the feasibility of this catalyst for practical environmental applications.

Acknowledgements: The Thermo FID-TG analyzer and MultiGas FTIR Gas Analyzer 2030G under the project No. BG16RFPR002-1.014-0006 "National Center of Excellence Mechatronics and Clean Technologies "supported by the European Regional Development Fund under "Research Innovation and Digitization for Smart Transformation" program 2021–2027, was used for the experimental work. Research equipment of distributed research infrastructure INFRAMAT (part of the Bulgarian National roadmap for research infrastructures) supported by Bulgarian Ministry of Education and Science was also used in the investigation.

The role of Carbon-black in Composite Electrodes for Sodium Ion Batteries

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Keywords: Na-ion batteries, sodium titanates, anode materials

1. Introduction. Sodium ion batteries (NIBs) emerge as an attractive technology for large scale energy storage, while their lithium analogues (LIBs) are recognized as a exceptional technology for mobile energy storage [1]. The operation of both NIBs and LIBs relies on shutteling of Na^+ or Li^+ ions between two electrodes via non-aqueous electrolyte. The electrodes are prepared by mixing of the active material with electrochemically inactive polymer binder and carbon-based conductive additive followed by casting on metal collectors. Conductive additives are of great importance when active materials have nano-morphology and/or low electron conductivity.

Herein, we examine the formation of composites between carbon black (Super C65) and sodium titanates with nanowire-like morphology [2]. The resulting composites were tested as electrode materials in model sodium-ion cells.

2. Experimental - Sodium titanates (NTO) were hydrothermally synthesized using high-pressure laboratory reactor Berghof, BR-100. The electrochemical characterization was carried out in model sodium ion cells versus Na metal as anode and 1M $NaPF_6$ in PC The electrodes were fabricated by mixing of active mass with carbon black (Super C65) and carboxymethyl cellulose (CMC) in ratios of 80:10:10 and 70:20:10, respectively.

3. Results and Discussion – A uniform coating of $Na_2Ti_6O_{13}$ nanowires with carbon was achieved by mixing carbon black with sodium titanate. In half sodium ion cells, composites between sodium titanates and C65 store sodium predominately by capacitive and faradaic reactions, as a result of which the phase composition and structure of titanates are retained. Sodium titanates display good cycling stability and exceptional rate capability. At a rate of C/2, composite with 12 wt. % C65 delivers a reversible capacity of 160 mAh/g, which is higher than that of the composite richer on C65 (i.e. 125 mAh/g for the composite with 22 wt. % C65). By increasing the charging rate from C/2 to 5C, the better performance of carbon-poor composite is preserved, reaching a capacity of around 65 mAh/g.

4. Conclusions. We have demonstrated that carbon black forms flexible composites with sodium titanate nanowires. These composites serve as electrodes in sodium ion cells since they deliver high capacity and exhibit good cycling stability. For sodium titanate nanowires, the best performance is achieve when the amount of carbon black is of 12 wt.%.

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Composites for Thermoelectric Devices Based on Reduced Graphene

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Keywords: Thermoelectric oxides, reduced graphene, composites

In the recent years there has been an extensive research in materials which can convert energy in efficient and affordable manner. In this aspect, the most intriguing materials comprise the misfit layered oxides, $Ca_3Co_4O_9$. Because of their flexible structures accommodating cobalt in different oxidation state, $Ca_3Co_4O_9$ exhibits good thermoelectric properties. Thus, $Ca_3Co_4O_9$ is recognized as effective thermoelectric materials. For practical applications, it is necessary to improve the thermoelectric efficiency of $Ca_3Co_4O_9$ especially at room temperature. In this study, we propose the formation of composites between reduced graphene oxide (rGO) and $Ca_3Co_4O_9$ as an effective experimental way to improve performance in thermoelectric devices. rGO is chosen due to its relatively good electrical conductivity.

The reduced graphene oxide (rGO) and N-doped analogue (NrGO) are commercial products provided by Graphit Kropfmühl GmbH (Germany). The composites were fabricated through ball milling, the amount of graphene additives was varied between 1 and 20 wt.%.

The thermoelectric efficiency was evaluated on the basis of measured electrical resistivity, Seebeck coefficient and thermal conductivity at room temperature. Among the carbon-based materials, both rGO and NrGO are characterized by extremely low thermal conductivities, but their figures of merit remain small. A comparison shows that NrGO outperforms the rGO, thus motivating the use NrGO as a component in multiphase composites. The addition of small amount of NrGO to $Ca_3Co_4O_9$ (i.e. 2 wt. %) leads to an improvement in the thermoelectric activity of to $Ca_3Co_4O_9$. This is a result of the simultaneous decrease in the thermal conductivity and preservation of the Seebeck coefficient.

This study reports the beneficial effect of the rGO when is used as component in thermoelectric devices and sodium-ion batteries. The correlations established between the thermoelectric and electrochemical properties of composites and their morphology and the amount of individual components could be used for further optimization of the performance of oxides as thermoelectric materials.

Acknowledgements: This work was supported by European Regional Development Fund under "Research Innovation and Digitization for Smart Transformation" program 2021-2027 under the Project BG16RFPR002-1.014-0006 "National Centre of Excellence Mechatronics and Clean Technologies".

Hydrothermal amino acids formation: an *ab initio* approach

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Keywords: prebiotic chemistry, hydrothermal conditions, sulfur-containing amino acids

The question about amino acids formation on the Early Earth under hydrothermal conditions is a fascinating topic in the prebiotic chemistry field. The related modern investigations are based on the pioneer work of Urey and Miller, published on May 15, 1953 in *Science*. Their series of experiments elegantly show the amino acids formation from simple molecules, using as an energy source heat and electric sparks (mimicking lightning).

The proposed hypothesis assumes that the initial molecules were H_2O, HCN, and H_2S, which were available under hydrothermal conditions. Starting from them, an original reaction mechanisms and reaction pathways for the amino acids formation are suggested. We propose the reactions cascade, leading to the following amino acids generation – glycine, alanine and serine, as well as sulfur-containing ones – cysteine and homocysteine. The investigations were carried out by means of quantum-chemical calculations at SMD/SCS-MP2/cc-pVDZ level of the theory.

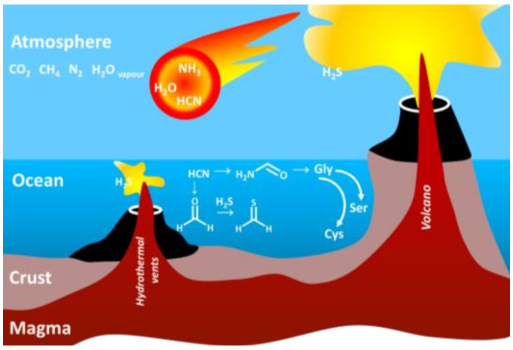

Figure 1. Prebiotic conditions on the Early Earth: simple precursors and some key amino acids formation in the Ocean under hydrothermal conditions.

As a result, *ab initio* quantum-chemical calculations provide an insight into original reaction mechanisms for alanine, serine, cysteine and homocysteine formation from glycine. The results confirm kinetically preferable formyl glycine formation in comparison with cysteine and serine. Moreover, the present schematic potential energy profiles along the reaction pathways for alanine, serine, cysteine and homocysteine demonstrate that their formation also takes place, since the considered reactions are exothermic.

Acknowledgements: The Bulgarian National Science Fund within the financial support for project of junior basic researchers and postdocs – 2021 (contracted as КП-06-М59/3) is acknowledged for the financial support for this investigation. We also thank the provided access to the e-infrastructure of the National Center for Regional Education - part of the Bulgarian National Roadmap for Regional Education, financially coordinated by the Ministry of Education and Science of the Republic of Bulgaria (Grant No. D01-325/01.12.2023).

Characterization and phototcatalytic properties of sol-gel prepared $SrFe_{1-X}Ti_XO_3$ (x = 1, 0.85, 0.15)

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Keywords: photocatalysis, sol-gel synthesis

With recent industrial progress, water pollution has escalated into a worldwide concern. Among the many pollutants, pharmaceutical compounds—particularly antibiotics—pose a serious threat due to their potential to promote antibiotic resistance in humans. Sunlight-driven heterogeneous photocatalysis has emerged as a promising approach for breaking down these contaminants, offering both cost efficiency and environmental sustainability. As a result, the development of advanced photocatalysts is a key focus for researchers globally.

In this work, $SrFe_{1-x}Ti_xO_3$ (x = 1, 0.85, 0.15) samples were synthesized using the sol-gel method. Their structural, morphological, and optical characteristics were analyzed through various techniques, including UV-Vis and IR spectroscopy, Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD). The photocatalytic performance of these materials was evaluated by testing their ability to degrade tetracycline hydrochloride in distilled water under different light conditions—sunlight, UV, and visible light. Notably, the samples demonstrated enhanced catalytic activity under sunlight exposure (Fig. 1).

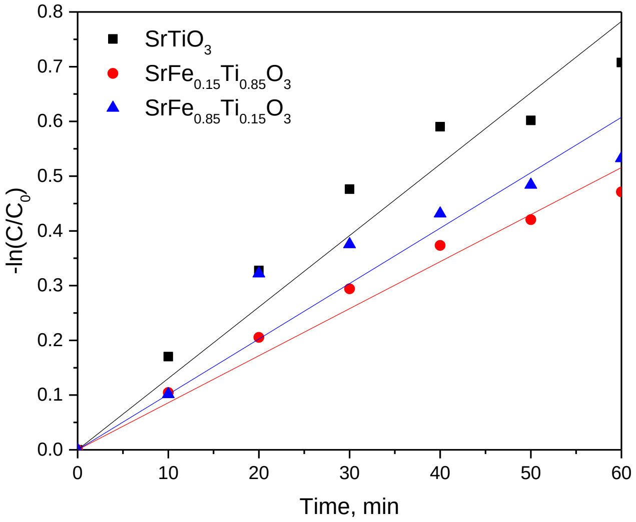

Fig. 1 Kinetics of sunlight illuminated photocatalytic degradation of Tetracycline hydrochloride by $SrFe_{1-X}Ti_XO_3$ (x = 1, 0.85, 0.15) nanopowders

Theoretical and Experimental Studies on the Conversion of Gypsum from Flue Gas Desulfurization into Calcium Hydroxide

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Keywords: thermodynamic simulation, Pitzer model, CaSO4·2H2O conversion, Calcium hydroxide

A huge amount of waste gypsum is generated annually from the flue gas desulfurisation processes used in power plants and industrial facilities, leading to environmental pollution, including soil degradation and water contamination. That is why finding methods for its efficient recycling is the subject of ongoing research.

The present work aimed to design an effective method for the conversion of gypsum from power plant flue gas desulfurization into calcium hydroxide, based on theoretical considerations. For this purpose, a thermodynamic simulation of the stable and metastable equilibria in the four-component system Na^+, Ca^{2+}/OH^-, $SO_4^{2-}//H_2O$ at 25 °C was performed using the ion-interaction Pitzer model. Crystallization of three stable compounds – $Ca(OH)_2$, $CaSO_4{\cdot}2H_2O$ and $Na_2SO_4{\cdot}10H_2O$, and three metastable salts – $2Na_2SO_4{\cdot}CaSO_4{\cdot}2H_2O$, $Na_2SO_4{\cdot}CaSO_4$ and Na_2SO_4, was calculated. The largest are the crystallization fields of $Ca(OH)_2$ and $CaSO_4{\cdot}2H_2O$, bisecting the solubility diagram into two almost equal parts. Simulation of the $CaSO_4{\cdot}2H_2O$ conversion process with NaOH solutions of different concentrations showed that increasing the NaOH concentration and the excess over $CaSO_4{\cdot}2H_2O$ would lead to possible co-crystallization of metastable salts and contamination of the final product.

Experimental studies have been conducted to optimise the conversion process, as not only thermodynamic but also kinetic factors influence it. The solution concentration and excess of the NaOH, the method of its introduction, the time of stirring and the maturation of the suspension were varied. It was found that 2M NaOH added at once, 2h stirring, and 22h maturation are the optimal. The highest degree of conversion (94%) is obtained at 25% excess of NaOH. At 10% excess the conversion is 91%, and at 5% excess – 88%. This shows that the most economically advantageous process is at a 5-10% excess of NaOH.

The possibility of capturing CO_2 from the air under static conditions with the potential use of the obtained $Ca(OH)_2$ as a lime plaster was tested. It was found that the best result was obtained with a wetted sample with the addition of xanthan gum (0.36% of the mass of the $Ca(OH)_2$ sample), which retains moisture in the material for a longer time and thus increases its reactivity.

Acknowledgements: The research was conducted within the framework of "National Centre of Excellence Mechatronics and Clean Technologies", project № BG16RFPR002-1.014-0006, supported by European Regional Development Fund under "Research Innovation and Digitization for Smart Transformation" program 2021-2027

UV-Activated gas sensor elements based on composite metal-oxide nanostructures

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Keywords: metal oxides, nanostructures, PLD, open air, UV-activated sensors

Resistive-type gas sensors based on semiconductor metal oxides are the most widely used sensors due to their low cost, easy production, compact size and simple measurement electronics. The detection mechanism is based on the change of the sensor element's resistance as a function of the surrounding atmosphere. One effective way to improving the performance of the sensors is UV light activation of the sensor surface, which, on the one hand, changes the kinetics of the surface processes and, on the other, allows the development of low-power and low-cost portable devices. Semiconductor metal oxides, particularly ZnO and SnO_2 are suitable candidates for UV-activated sensors since they are sensitive to exposure to various harmful and air-polluting gases and demonstrate photosensitive properties.

In this work, we present the fabrication of composite metal-oxide nanostructures designed for UV-activated gas sensors. The sensor elements were produced by pulsed laser deposition carried out in air at atmospheric pressure, also known as PLD in open air or atmospheric PLD. The physical process on which the PLD is based is laser ablation of a solid-state target. When this technology is performed at atmospheric pressure, porous nanoparticle structures are formed due to the fast condensation of ablated species close to the target. Such structures possess a high surface-to-volume ratio, which is a major characteristic concerning the gas sensor response. The nanostructures were formed by laser ablation of ceramic targets synthesised of ZnO (SnO_2) and a small amount of 5 or 10 wt% SnO_2 (ZnO) metal oxides. The samples' structure, morphology, optical, electrical, and photosensitive properties were studied. It was found that a composite structure consisting of ZnO or SnO_2 and mixed ZnO-SnO_2 metal oxides was formed during the ablation process. The morphology of the composites does not significantly differ from the morphology of the pure ZnO or SnO_2 metal oxide. All samples possess photosensitive properties, i.e., their electrical properties depend on the UV irradiation, which makes them a suitable candidate for light-sensitive gas sensor elements.

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Sol-gel processing of Eu^{3+} doped SiO_2-B_2O_3 glasses

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Keywords: sol-gel, glasses, properties

The application of sol-gel processing methods for preparing glasses has been receiving considerable attention because it provides a means of obtaining glasses of unusual compositions, high purity, and good homogeneity at temperatures significantly lower than required in conventional processing. Additionally, this method allows also overcoming some problems such as liquid immiscibility especially in systems containing B_2O_3. It is well known that glasses from the SiO_2-B_2O_3 systems are difficult to produce by the conventional melting process because of excessive volatilization of B_2O_3 from the melts and extremely high melting temperatures. The existence of such complications makes the sol-gel method a suitable and reproducible route for obtaining of new materials with interesting properties.

Glasses from the SiO_2-B_2O_3 binary system containing up to 20 mol% B_2O_3 have been synthesized. These glasses have been characterized by X-ray diffraction, UV-Vis and IR spectroscopy. In order to obtain a homogeneous glass, it was determined that a certain degree of hydrolysis of $Si(OC_2H_5)_4$ was essential before $B(OC_2H_5)_3$ could be incorporated. According to the XRD method, amorphous gels have been obtained. IR spectra exhibited bands in the 1700 - 620 cm^{-1} range which could be related to the vibrations of O-Si-O, Si-O-Si, B-O, and Si-O-B bonds.

Figure 1. Sol-gel derived Eu^{3+} doped SiO_2-B_2O_3 glass.

Charge Transfer or Energy Transfer: the Effect of Diethyldithiocarbamate Ligand on the Luminescent Emission of Eu^{3+} and Sm^{3+}

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Keywords: europium, samarium, diethyldithiocarbamate, excited states, TDDFT

First principles quantum chemistry calculations were implemented to elucidate the sensitization mechanism of Eu^{3+} and Sm^{3+} luminescence within the molecules of $Ln(S_2CR)_3$Phen complexes (where Ln ≡ Eu,Sm; Phen ≡ 1,10-phenanthroline, R ≡ $N(C_2H_5)_2$). In preceding publications, dithiocarbamates have been studied and applied sucessfully as suitable precursors for the production of lanthanide sulphide nanoparticles used in photocatalysis. It has been demonstrated that $Ln(S_2CR)_3$Phen could also be suitable materials for novel electronic devices. At the same time, the combination of Phen and dithiocarbamate (dtc^-) ligands act as a better 'antenna' for Sm^{3+} and Pr^{3+} ions, in contrast to the corresponding complexes of Eu^{3+}, Tb^{3+} and Dy^{3+} ions. The emergence of charge transfer (CT) states in the excitation spectra of europium complexes with dtc^- is one of the possible explanations.

To clarify further the mechanism of electronic relaxation and energy transfer in the $Ln(S_2CR)_3$Phen compounds, DFT/TDDFT/ωB97xD method with perturbative spin−orbit coupling corrections has been applied in order to reproduce the geometry and electronic wavefunctions at the energy minima of ground (S_0), first singlet (S_1) and first triplet (T_1) excited states. In all cases the S_1 state demonstrates an ILCT character, in contrast to earlier suggestions. Similar electronic relaxation paths and a suitable energy gap between ligand-centered donor and metal-centered acceptor states were identified in all complexes. The weak emission of $Eu(S_2CR)_3$Phen was explained after comparison with corresponding experimental data.

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Effect of the synthesis procedure of bio-derived hard carbon on the sodium storage

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Keywords: bio-waste, bio-derived hard carbon, sodium-ion storage, sustainable energy storage

Recycling bio-waste from households and converting it into reusable materials is one of the main goals of environmentally sound waste management. Due to its high carbon content, bio-waste is a valuable raw material for the production of carbon materials such as activated carbon, graphite, etc.

Here we reveal the potential of hard carbon derived from walnut shells as a promising electrode material for sodium ion storage. Furthermore, we examine the effect of the synthesis procedure on the textural features of the obtained samples and their electrochemical properties. For this purpose, we obtained hard carbon in three ways - through torrefaction, preliminary acid treatment of the raw material, and hydropyrolytic. Thus obtained carbons are subsequently pyrolyzed under argon at 1300 ^{o}C. The influence of the synthesis procedure on the textural features of the samples was investigated using BET and HR-TEM. The electrochemical properties of bio-derived hard carbons were analysed in model Na-ion cells with carbonate-based sodium electrolyte. To quantify the Na-storage performance, we determined four parameters: reversible specific capacity, first irreversible capacity, cycling stability and rate capability. Based on the above results, it is established that the hard carbon, obtained via acid pretreatment outperforms all others.

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High-entropy spinel oxides as catalyst for Low –Temperature Hydrocarbon Oxidation

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Keywords: High-entropy oxides, combustion synthesis, catalysis, hydrocarbons

In the present study, the solution combustion synthesis method is used for the preparation of nanosized high-entropy spinel oxides. Materials with composition $(CoMnFeNiT)_3O_4$, where T = (Cr, Zn, Al), were synthesized using sucrose as a fuel in the combustion reaction. The resulting materials are characterized by X-ray diffraction (XRD) and Mössbauer spectroscopy. The materials were tested as catalysts in the reaction of hydrocarbon oxidation. The XRD shows a single-phase spinel for all samples with an average size below 15nm. Mössbauer spectra of three samples show two doublets corresponding to Fe3+. The Db1 doublets, with lower quadrupole splitting values, can be attributed to iron ions in a more symmetrical environment. The Db2 doublets are probably due to iron in “more defective” positions. The catalytic properties of the high-entropy oxides with composition $(CoMnFeNiCr)_3O_4$, $(CoMnFeNiAl)_3O_4$ and $(CoMnFeNiZn)_3O_4$ were investigated by the reactions of complete catalytic oxidation of methane, ethane, propane, butane, and CO (Fig.1). The catalytic test shows that the lowest value for T50 (T50 = 64°C) were observed for the combustion of CO on $(CoMnFeNiAl)_3O_4$, followed by (T50 = 82°C) on $(CoMnFeNiZn)_3O_4$ and (T50 = 180°C) on $(CoMnFeNiCr)_3O_4$, respectively. It should be noted that in all catalytic reactions, $(CoMnFeNiAl)_3O_4$ spinel is more active than these having $(CoMnFeNiCr)_3O_4$ and $(CoMnFeNiZn)_3O_4$.

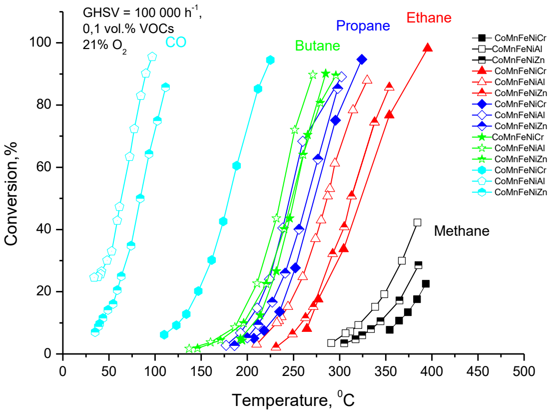

Figure 1. Dependencies of the conversion on the reaction temperature during complete oxidation of different hydrocarbons on $(CoMnFeNiCr)_3O_4$, $(CoMnFeNiAl)_3O_4$ and $(CoMnFeNiZn)_3O_4$.

Acknowledgements: The authors are thankful to Project КП-06-М89/3"Synthesis and characterization of High-entropy spinel oxides with applications in catalysis".

Synthesis and catalytic activity of spinel oxides $(CoMnFeNiCr)_3O_4$, with different entropy

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Keywords: High-entropy oxides, combustion synthesis, complete oxidation

In the present study was synthesized and characterized high-entropy spinel oxides $(CoMnFeNiCr)_3O_4$ with stoichiometric ratio 1:1:1:1:1 and 1:1:2:1:1. The solution combustion synthesis method was use for the preparation of high-entropy spinel oxides. The as-prepared samples were treated for 1 h at 400°C. Structural and morphological characteristics of samples are obtained by powder X-ray diffraction (XRD), Mössbauer spectroscopy, and Low-temperature nitrogen adsorption (BET). XRD result show the formation of single-phase materials for both samples with a crystallite size of 5nm. Mössbauer spectra of both samples show doublets corresponding to Fe3+. The Db1 doublets, with lower quadrupole splitting values, can be attributed to iron ions in a more symmetrical environment. The Db2 doublets are probably due to iron in “more defective” positions. The BET results show a specific surface area of about $30 m^2/g$ for both samples. Catalytic tests in complete oxidation reactions of hydrocarbons (methane, ethane, propane, etc.) of the obtained high-entropy materials were carried out in a multi-reactor automated system (Fig1). The lowest values for the temperature for 50% conversion are achieved in the complete oxidation of CO (T50 = 179°C) on for stoichiometric sample and (T50 =190°C) on for the non-stoichiometric sample. It should be noted the slight decrease in the catalytic activity in the complete oxidation of ethane, propane, butane and CO on non-stoichiometric sample, the temperatures for 50% conversion are 10–20 °C higher than those on stoichiometric sample.

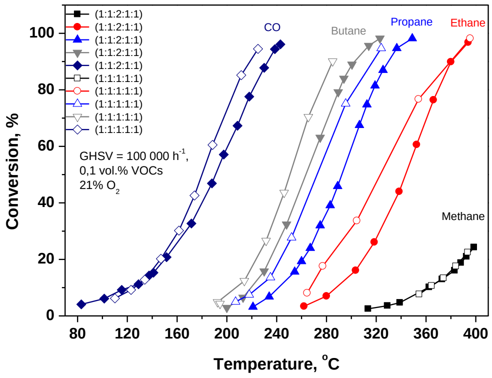

Figure1.Dependencies of the conversion on the reaction temperature during complete oxidation of different hydrocarbons on $(CoMnFeNiCr)_3O_4$ with stoichiometric ratio 1:1:1:1:1 and 1:1:2:1:1.

Acknowledgements: The authors are thankful to Project KP-06-M89/3 "Synthesis and characterization of High-entropy spinel oxides with applications in catalysis".

Preliminary Investigation of Commercial Amino-Functionalized Adsorbents for Direct Air Capture of CO_2

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Keywords: amino-functionalized adsorbents, FTIR spectroscopy, solid-state NMR, DAC, TVSA

This study aimed to identify commercially available adsorbents suitable for direct CO_2 capture from air (DAC) in a modular system based on cyclic adsorption-desorption processes involving temperature and vacuum swing (TVSA).

Three amino-functionalized sorbents were selected and studied: two mesoporous silica materials with pore sizes of 2 nm (A-MCM-48) and 6 nm (A-SBA-15), both purchased from Sigma-Aldrich, and an anion exchange resin (Lewatit), purchased from Supelco.

FTIR spectroscopy revealed the presence of NH_2, CH_2, and CH_3 groups on the mesoporous silica materials. Solid-state NMR analysis has indicated that the grafted moieties are most likely –$(CH_2)_3NH_2$ groups. Additionally, the FTIR data suggest that most of the surface silanol groups were involved in the functionalization with alkylamine groups. The Lewatit resin is a polystyrene-based material, also functionalized with primary amines. Notably, such amines are known to exhibit superior CO_2 capture performance under DAC conditions.

All tested amino-functionalized sorbents exhibited chemical affinity toward CO_2, adsorbing it predominantly in the form of ammonium carbamate, with minor contributions from carbamic acid. Among them, the resin demonstrated significantly higher CO_2 uptake compared to the mesoporous silicas. Notably, the chemisorbed CO_2 on the resin remained stable under dynamic vacuum at room temperature, consistent with its considerably higher isosteric heat of adsorption. These findings suggest that the resin holds greater potential for integration into DAC systems employing TVSA technology.

Nevertheless, further optimization of the amine type, amine loading, and support nature may be required to achieve a favorable balance between adsorption capacity, regeneration energy, and long-term durability.

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