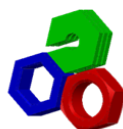




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# BULGARIAN ACADEMY OF SCIENCES



GEORGI NADJAKOV  
INSTITUTE OF SOLID STATE PHYSICS



## BOOK OF ABSTRACTS

**NCMCT Workshop on Advanced Materials & Technologies**

**Meridian Hotel Bolyarski, Veliko Tarnovo**

**February 28<sup>th</sup> – March 1<sup>st</sup>, 2023**

National Center of Mechatronics and Clean Technologies ([www.cemct.eu](http://www.cemct.eu)), Project **BG05M2OP001-1.001-0008** funded by the Operational Program Science and Education for Smart Growth 2014-2020, co-financed by the European Union through the Regional Development Fund ([www.eufunds.bg](http://www.eufunds.bg)).

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BULGARIAN ACADEMY OF SCIENCES  
GEORGI NADJAKOV INSTITUTE OF SOLID STATE PHYSICS  
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February 28<sup>th</sup> – March 1<sup>st</sup>, 2023

## PROGRAM

### February 27<sup>th</sup> (Monday)

17:00 – 18:00 Registration  
18:00 – 20:00 Cocktail

### February 28<sup>th</sup> (Tuesday)

09:30 – 09:40 Opening Ceremony

**09:40 – 11:00 Chair: H. Chamati**

09:40 – 10:20 N. Drenchev, K. Chakarova, M. Mihaylov, E. Ivanova, L. Dimitrov, H. Aleksandrov, G. Vayssilov and K. Hadjiivanov, Adsorption of CO<sub>2</sub> on cation-exchanged FAU zeolites

10:20 – 11:00 E. Guziewicz, Atomic layer deposition as a growth method for advanced materials

**11:00 – 11:20 Coffee break / Collective photo**

**11:20 – 12:20 Chair: A. Dinescu**

11:20 – 11:40 K. Maksimova -Dimitrova, G. Borisov, E. Lefterova and E. Slavcheva, Composite catalysts on interactive oxide support for alkaline water electrolysis

11:40 – 12:00 I. Bineva, D. Nesheva, B. Valdez-Salas, M. U. Grujić-Brojčin and M. J. Šćepanović, Morphology control and enhanced sensitivity of thin film semiconductor oxides-based gas sensors: a fractal analysis study

12:00 – 12:20 V. Dzhurkov, D. Spasov, A. Paskaleva and D. Nesheva, Gas sensor test equipment Kenosistec KGAS4S. How does it work and areas of application?

**12:20 – 14:00 Lunch break**

**14:00 – 16:00 Chair: M. Šćepanović**

14:00 – 14:40 I. M. Szilágyi, Marcell Bohus, Z. I. Varady and T. Leba, Hybrid and composite oxide and carbon nanofluids

14:40 – 15:20 V. Donchev and M. Milanova, Dilute nitrides heterostructures grown by liquid phase epitaxy for solar cells applications

15:20 – 15:40 D. Nesheva, R. Gegova-Dzhurkova, I. Stambolova, K. Zaharieva, and V. Dzhurkov, Improving the photocatalytic and sensing properties of sol-gel ZnO thin films by modifying the way of preparation

15:40 – 16:00 S. Boyadjiev, B. Blagoev, D. Delibatov, V. Mehandzhiev, P. Terziyska, I. Avramova and P. Rafailov, Characterization of graphene and ALD grown Al<sub>2</sub>O<sub>3</sub>/graphene heterostructure

16:00 – 18:00 Poster Session

**March 1st** (Wednesday)

**09:30 – 10:50** **Chair: D. Nesheva**

09:30 – 10:10 M. Šćepanović and M. Grujić-Brojčin, Effects of laser power and excitation wavelength on the Raman spectra of nanostructured materials

10:10 – 10:50 A. Dinescu, M. Dragoman, A. Muller, A. Baracu and A. Avram, field emission scanning electron microscopy for nanoscale fabrication

**10:50 – 11:10** **Coffee break**

**11:10 – 12:30** **Chair: E. Guzewicz**

11:10 – 11:30 M. Shehadi, S. Karatodorov, L. Stoychev, D. Tsankov and T. Petrov, Measurement of nonlinear optical characteristics of wide bandgap semiconductor AlN using modified femtosecond z-scan method

11:30 – 11:50 P. M. Rafailov, C. Thomsen, M. M. Gospodinov, P. K. Sveshtarov, V. B. Mehandzhiev and D. Z. Dimitrov, Raman characterization of low-dimensional nanostructures and single crystals

11:50 – 12:10 E. Iordanova, G. Yankov, H. Chamati and L. Kovachev, Compression of neutral particles by an optical lens

12:10 – 12:30 G. Borisov, N. Borisov, J. Heiss, U. Schnakenberg and E. Slavcheva, Thin Pt films as catalysts for electrochemical hydrogen compression

**12:30 – 14:00** **Lunch break**

**14:00 – 15:20** **Chair: I. M. Szilágyi**

14:00 – 14:40 A. Paskaleva and D. Spassov, Challenges to optimize charge trapping non-volatile flash memories cells with HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks

14:40 – 15:20 S. Banerjee, Towards an expanded palette of materials and mechanisms for neuromorphic computing

**15:20 – 15:30** **Closing Ceremony**

## POSTER PRESENTATIONS

1. A. Stoyanova, B. Karamanova and S. Veleva, The impact of physicochemical characteristics of carbon materials on the capacitive performance of symmetric supercapacitors with alkaline electrolyte.
2. B. Abrashev, V. Terziev, M. Pandev, D. Levi, M. Slavova and K. Petrov, Novel structure of composite gas-diffusion electrode (CGDE), containing zeolite for rechargeable metal hydride (MH)-air batteries.
3. G. Yankov, N. Stankova and E. Iordanova, The effects of ultrafast laser pulses on the properties of advanced medical-grade PDMS polymer.
4. V. Mankov, G. Dyankov, E. Hikova and H. Kisov, SPR sensors biochips based on protected silver/copper layers.
5. P. Karakashkova, V. Serga, G. Tyiliev and S. Minkovska, Synthesis and characterization of TiO<sub>2</sub>/WO<sub>3</sub> nanocomposites with enhanced photocatalytic activity.
6. O. Kostadinova, K. Banov and S. Stankov, Raman spectroscopic evidence for multiphase composition in copper tin sulfides.
7. P. Vassileva, I. Uzunov and D. Voykova, Kinetics, equilibrium and thermodynamics of Congo red removal by cationized materials based on agricultural waste.
8. G. B. Hadjichristov and S. Minkovska, Optical spectroscopy of photochromic fluorescent spirooxazines sensitive to metal ions.
9. B. Mladenova, G. Borisov and E. Slavcheva, Highly efficient catalyst applicable in electrochemical hydrogen pump/compressor.
10. S. Stankov, O. Kostadinova, I. Popov, H. Kolev and T. Petkova, Physicochemical and electrocatalytic properties of non-stoichiometric Ba<sub>2</sub>Sr<sub>2</sub>La<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> perovskites.
11. S. Veleva, B. Karamanova, A. Stoyanova and A. Arenillas, Electrochemical properties of carbon xerogel-based supercapacitors using non-aqueous electrolytes.
12. G. B. Hadjichristov, Y. G. Marinov and T. E. Vlakhov, Nematic liquid crystals/polymer composites as ion conductors.
13. V. Terziev, B. Abrashev and K. Petrov, Electrochemical investigation of carbon based gas diffusion electrodes (GDEs) for rechargeable metal hydride (MH)-air battery.
14. B. Karamanova, A. Stoyanova and A. Aliosmanova, Effect of the conductive additives on the capacitive performance of symmetric supercapacitors based on activated carbon in alkaline electrolyte.
15. E. Petkucheva, G. Borisov, B. Mladenova, H. Penchev, F. Ublekov and E. Slavcheva, Materials, structure, function and possibilities of AEM-URFCs.
16. V. Nikolov, I. Koseva, P. Ivanov, M. Gancheva, P. Tzvetkov, P. Petrova and R. Tomova, Europium doped germanate glass-ceramics containing Ca<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub> as a main phase for potential red phosphor application.
17. I. Dionisiev, P. Rafailov, B. Babeva, K. Buchkov, V. Videva, V. Strijkova, Hr. Dikov, V. Marinova and D. Dimitrov, Structural characterizations of 2D tungsten diselenide.
18. I. Tsacheva, O. Dimitrov, M. Dimitrova, A. Gigova and D. Uzun, Microwave-assisted synthesis of phosphorus containing composites as functional electrocatalytic materials.
19. N. Bozhanova, V. Zhelev, O. Kostadinova, M. Dimitrova, O. Dimitrov, V. Ilcheva, V. Boev and T. Petkova, Structural characterization of Ce<sub>1-x</sub>Sm<sub>x</sub>O<sub>2-x/2</sub> powders prepared by ionic gelation and high temperature techniques.
20. N. Minev, P. Rafailov, V. Videva, V. Strijkova, I. Avramova, I. Dionisiev, K. Buchkov, Hr. Dikov, D. Dimitrov and V. Marinova, Low temperature synthesis of PtSe<sub>2</sub> and PtTe<sub>2</sub> nanolayers.

21. B. Drenchev, V. Boev, L. Soserov, V. Ilcheva, M. Dimitrova, O. Dimitrov and A. Stoyanova, Transformation of powder-pasted and electroplated zinc active mass after cycling in Ni-Zn battery cells.
22. V. Zhelev, O. Kostadinova, S. Stankov, K. Banov, P. Petkov and T. Petkova, Investigation of the physicochemical and electrochemical behaviour of heat-treated shungite.

**ABSTRACTS  
INVITED LECTURES**

## Adsorption of CO<sub>2</sub> on cation-exchanged FAU zeolites

N. Drenchev<sup>1</sup>, K. Chakarova<sup>1</sup>, M. Mihaylov<sup>1</sup>, E. Ivanova<sup>1</sup>, L. Dimitrov<sup>1</sup>,  
H. Aleksandrov<sup>1,2</sup>, G. Vayssilov<sup>2</sup> and K. Hadjiivanov<sup>1\*</sup>

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In order to design efficient CO<sub>2</sub> capture materials, it is necessary to ensure a high adsorption capacity. Cation-exchanged zeolites are promising materials for this purpose because the exchanged cations can often attach two or even three small molecules [1]. To ensure a high concentration of exchanged cations, we choose to use FAU zeolites (X and Y). It was found that up to an equilibrium CO<sub>2</sub> pressure of 200 mbar and at ambient temperature, one Na<sup>+</sup> site in NaY zeolite can attach only one CO<sub>2</sub> molecule. Lowering the temperature in the presence of CO<sub>2</sub>, however, leads to formation of geminal species, Na<sup>+</sup>(CO<sub>2</sub>)<sub>2</sub>. All this can be easily monitored by *in situ* infrared spectroscopy following the evolution of the ν(<sup>13</sup>CO<sub>2</sub>) band appearing as a result of the <sup>13</sup>C natural abundance: it is detected at 2288–2285 cm<sup>-1</sup> for the Z–Na<sup>+</sup>...OCO complexes and at 2280–2279 cm<sup>-1</sup> for the geminal Z–Na<sup>+</sup>(OCO)<sub>2</sub> species (Z stands for zeolite). Unfortunately, the process is not suitable for practical use because it occurs at a low temperature. We therefore decided to change the nature of the exchanged cation. We chose Ca<sup>2+</sup> because of its high electrophilicity and the reported ability to bind three CO molecules when in appropriate positions in zeolites [1]. When CO<sub>2</sub> is adsorbed on CaNaY at ambient temperature and pressure of ca. 0.1 mbar, linear Z–Ca<sup>2+</sup>...OCO species are formed (ν(<sup>13</sup>CO<sub>2</sub>) at 2298 cm<sup>-1</sup>). Increasing the equilibrium pressure, however, leads to the formation of Z–Ca<sup>2+</sup>(CO<sub>2</sub>)<sub>2</sub> geminal complexes (ν(<sup>13</sup>CO<sub>2</sub>) at 2294 cm<sup>-1</sup>), which predominate at P > 1 mbar. Lowering the temperature leads to the formation of triligand Z–Ca<sup>2+</sup>(CO<sub>2</sub>)<sub>3</sub> adducts (ν(<sup>13</sup>CO<sub>2</sub>) at 2291 cm<sup>-1</sup>). They are also produced at ambient temperature and pressure above 65 mbar. Importantly, a water molecule adsorbed on the Z–Ca<sup>2+</sup> site does not block the formation of complexes with CO<sub>2</sub>. On the contrary, Z–Ca<sup>2+</sup>(H<sub>2</sub>O)(CO<sub>2</sub>) and Z–Ca<sup>2+</sup>(H<sub>2</sub>O)(CO<sub>2</sub>)<sub>2</sub> species have been identified. This allows CO<sub>2</sub> capture even in the presence of a moderate amount of water. The experimental results were confirmed by DFT calculations. Our findings indicate that CaFAU zeolites can be very effective CO<sub>2</sub> capture materials. Studies with CaX zeolite (allowing higher Ca<sup>2+</sup> loading and hopefully higher CO<sub>2</sub> adsorption capacity). are currently underway.

### References:

1. K. Hadjiivanov, E. Ivanova, M. Mihaylov and K. Chakarova. Adsorption of Two or More Molecules on One Cationic Center in Porous Materials. In *Comprehensive Guide for Mesoporous Materials, Vol. 2: Analysis and Functionalization*, Nova Science Publishers, New York, USA, 2015, pp. 269–288.

**Acknowledgements:** The experimental part of the work was supported by the National Science Fund of Bulgaria, Programme Vihren, Contract No KP-06-DV/1 from 2021.



## **Field Emission Scanning Electron Microscopy for nanoscale fabrication**

**Adrian Dinescu\***, Mircea Dragoman, Alexandru Muller, Angela Baracu, Andrei Avram  
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Many advances in fabrication processes at micro and nanoscale in the past two decades were possible due to field emission scanning electron microscopy, which is now an indispensable tool for analyzing and fabricating new nanostructures and nanomaterials.

The development of very efficient in-lens detectors for SEM and the capability to use low energy electron probes are the gateway to the revelation of new features and new properties of nanomaterials that have been hidden by the use of high accelerating voltages and large interaction of volume, in the high-resolution SEM (1,2).

Electron beams have been used for lithography for decades and pattern generators can be fitted to all modern SEMs, converting them in very powerful nanolithographic tools, without degrading or limiting their imaging capabilities. The SEM became a very versatile tool for micro and nanofabrication, the same equipment used for fabrication being used to view the resulting nanostructures.

To illustrate the patterning capabilities of electron microscopy, the second part of the talk will be focused on fabrication of a few nanoelectronic devices, like field effect transistors on graphene (3,4) and on SOI wafers for quantum computing or diffractive optical elements.

### **References:**

1. D.C Joy and D. Newbury, "Microscopy today", 10(2), 2002
2. I. Mullerova and L Frank, "Microscopy and Microanalysis 9 (suppl 3)", Microscopy Society of America (2003)
3. M. Dragoman, A. Dinescu, D. Dragoman, Nanotechnology, vol 25, no 41
4. M. Dragoman, A. Dinescu, D. Dragoman, , IEEE Transactions on Nanotechnology, Volume 17, Issue 2, March 2018, Pages 362-367

# Towards an Expanded Palette of Materials and Mechanisms for Neuromorphic Computing

Sarbajit Banerjee

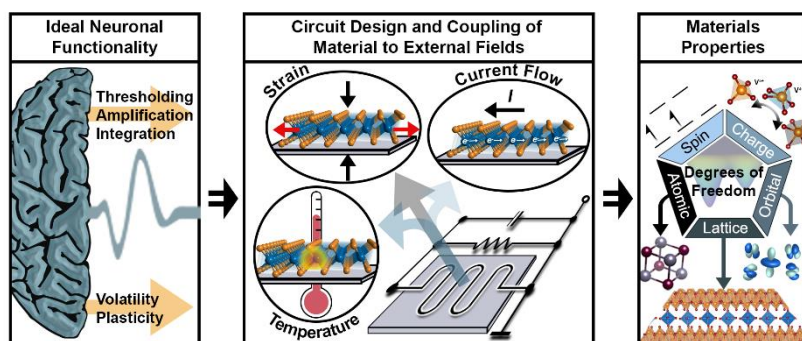
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The metal-insulator transitions of electron correlated transition metal oxides provide an attractive vector for achieving large conductance switching with minimal energy dissipation. However, given the sparse and disconnected current knowledge of neuromorphic materials, a fundamental understanding of descriptors of neuromorphic function formulated in terms of intrinsic material properties, and the influence of atomistic defects on mesoscale domain evolution in the presence of external applied fields is currently lacking. Using VO<sub>2</sub> and M<sub>x</sub>V<sub>2</sub>O<sub>5</sub> compounds as model systems, I will detail our efforts to develop a systematic understanding of how compositional modifications through substitutional or interstitial doping alter transformation characteristics such as the transition temperature, magnitude of switching, energy dissipation, and hysteresis.

The inclusion of dopant atoms strongly modifies the free energy landscapes in terms of relative phase stabilities, transformation barriers, and pathways; thereby profoundly altering the coupling of lattice, electronic, and spin degrees of freedom in a non-trivial manner. I will particularly focus on the three distinct mechanisms: (a) discovery of diffusive dopants that provide a distinctive new way to alter the dynamics of electronic transitions; (b) cation shuttling and polaron oscillation as a means of engendering metal—insulator transitions; and (c) lattice-anharmonicity-driven mechanisms in compounds with stereochemically active lone pairs.



**Figure 1:** We describe here an inverse design approach to identifying mechanisms and materials for neuromorphic computing.

## References:

1. Schofield, et al. Harnessing the Metal—Insulator Transition of VO<sub>2</sub> in Neuromorphic Computing. *Advanced Materials*, 2023, 2205294.
2. Sellers et al., An Atomic Hourglass and Thermometer Based on Diffusion of a Mobile Dopant in VO<sub>2</sub>. *Journal of the American Chemical Society*, 2020, 142, 15513–15526.
3. Parija et al., Metal-Insulator Transitions in β'-Cu<sub>x</sub>V<sub>2</sub>O<sub>5</sub> Mediated by Polaron Oscillation and Cation Shuttling *Matter* 2020, 2, 1166-1186. DOI: 10.1016/j.matt.2020.01.027.

**Acknowledgements:** Research supported as part of REMIND, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under DE-SC0023353

## **Challenges to optimize charge trapping non-volatile flash memories cells with HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stacks**

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Flash non-volatile memories (NVM) are the preferred choice for data storage in portable gadgets (tablets, smart phones, etc.) because they offer a small, low-power consuming and reliable alternative to disk storage. Up-to-now the dominant flash NVM technology was the floating gate memory cell in which the charge is stored in an electrically isolated poly-Si gate. However, the increasing demands for larger volumes of stored data causes an aggressive down-scaling of cell sizes and, consequently, the intrinsic limitations of floating gate technology become insurmountable. Charge trapping (CT) NVMs are a promising alternative to the conventional floating gate technology because they offer better operation characteristics, e.g. improved retention and endurance, lower power consumption, higher program/erase (P/E) speed. The current CT-NVMs are using Si<sub>3</sub>N<sub>4</sub> as a charge storage media and SiO<sub>2</sub> as blocking and tunnel oxides. HfO<sub>2</sub>-based dielectric materials have relatively high dielectric constant, large conduction band offsets with Si and tunnel oxide, and high trap densities, which made them a very attractive alternative to supersede the conventional Si<sub>3</sub>N<sub>4</sub>-based CT flash memories.

In this work we present investigations on metal/blocking oxide (BO)/high-k charge trapping layer (CTL)/tunnel oxide (TO)/Si (MOHOS) structures with HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-based CTL prepared by atomic layer deposition (ALD) from the view point of their application in CT-flash memories. The memory windows (representative for charge trapping), retention and endurance characteristics of the structures are studied in dependence on the stack composition, annealing process (rapid thermal annealing (RTA) in O<sub>2</sub>), material (SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>) and thickness of TO. Challenges to optimize density, energy and spatial distributions of charge storage traps, composition of charge trapping layer and thickness and material of tunneling oxide in order to meet the requirements for high density of trapped charge and reliable storage with negligible loss of charges in CT- flash memory cell are considered.

## Atomic Layer Deposition as a growth method for advanced materials

Elżbieta Guzewicz

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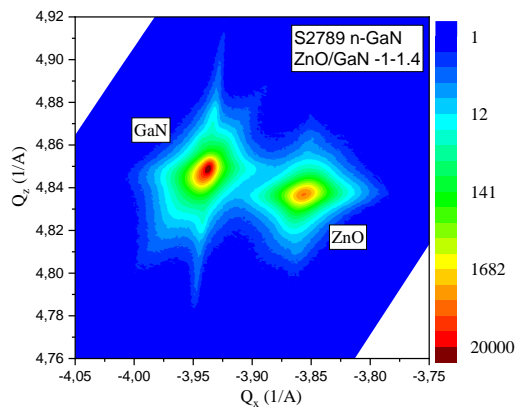
[guzel@ifpan.edu.pl](mailto:guzel@ifpan.edu.pl)

In recent years, Atomic Layer Deposition (ALD) has been increasingly used in science and industry, since it allows for obtaining very good quality materials at low prices of equipment and technological processes.

The main advantages of ALD technology are a low deposition temperature, uniform coverage of surfaces with highly developed morphology and possibility to cover large area substrates. For this reason, ALD can be used in industry for a variety of applications such as thermally unstable organic electronics and solar cells, where depositions over large areas is required. Because of a sequential growth and a related self-limited layer-by-layer deposition process it is possible to reproducibly grow thin films in a nanometer scale, which is crucial for gate dielectric applications in a new generation integrated circuits.

A variety of materials ranging from metallic to semiconducting and dielectric can be grown by ALD. In the lecture I will concentrate on zinc oxide, which is a widely investigated wide band-gap material for many applications such as light-emitting devices, sensors, transistors and transparent oxide for solar cells. Using the ALD technology we are able to obtain both polycrystalline and epitaxial ZnO films, conductive or highly resistive, adjusting the electrical, structural and optical parameters to the specific application.

**Acknowledgements** The presented work was supported by the Polish NCN Project DEC-2018/07/B/ST3/03576



The high-resolution XRD reciprocal space map (RSM) of epitaxial ZnO-ALD film deposited on GaN/Al<sub>2</sub>O<sub>3</sub> lattice-match substrate.

## **Hybrid and composite oxide and carbon nanofluids**

**Imre Miklós Szilágyi, Marcell Bohus, Zalán István Várady, Thong Le Ba**

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Heat exchangers are widely used in many energy related engineering applications, such as solar collectors, chemical industry, power production, waste heat recovery, air conditioning, automobile radiators and refrigeration. Although various techniques have been applied to enhance heat transfer, their performances are often limited by the low thermal conductivities of the heat transfer fluids. It has been proved that the dispersion of small amounts of nano-sized solid nanoparticles in base fluids enhance thermal conductivity. Nanofluids as a stable colloidal suspension are prepared by dispersing nanoparticles in base fluids to improve the thermal performance of heat transfer systems.

In this lecture, the thermal conductivity and viscosity of various single phase, hybrid and composite oxide and carbon nanofluids are presented. As solid nanomaterials for single phase nanofluids, halloysite nanotubes, SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles, carbon nanospheres and carbon nanopowders were used. For hybrid nanofluids, SiO<sub>2</sub>-TiO<sub>2</sub> were applied. For the first time, core/shell nanomaterials obtained by atomic layer deposition (ALD) were also tried to increase the thermal conductivity of nanofluids. The hybrid nanofluids were better in performance compared to the single phase ones. However, the ALD prepared core/shell ones were even more beneficial, which opens up a new way to obtain novel, beyond the state-of-the-art nanofluids.

## Dilute nitrides heterostructures grown by liquid phase epitaxy for solar cells applications

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There has been great interest in dilute nitride III-V-N materials (such as InGaAs(Sb)N, GaAsSbN) during the last two decades, driven in part by their potential application in multijunction (MJ) solar cells, which are expected to outperform single-junction devices. The research in this direction aims obtaining materials with a bandgap of the order of 0.8 - 1.2 eV, which are lattice matched to GaAs and can be used as an additional subcell in MJ solar cells. We present a comprehensive overview of the structural, optical and photoelectrical properties of GaAs-based dilute nitride materials grown by liquid-phase epitaxy (LPE) with a view of their photovoltaic applications. The possibility to incorporate nitrogen into the GaAs crystal lattice from a melt at nearly equilibrium conditions is demonstrated. Dilute nitride InGaAs(Sb)N and GaAsSbN epitaxial layers have been successfully deposited at temperatures lower than 600°C. X-ray microanalysis and X-ray diffraction have been used to determine the composition, lattice mismatch, and crystalline quality of the epitaxial layers. The morphology and surface roughness have been examined by atomic force microscopy. The extending of photosensitivity in the near-infrared region down to 1.33 eV for InGaAsN and 1.19 eV for GaAsSbN has been demonstrated by surface photovoltage spectroscopy at room temperature. The emission properties of as-grown dilute nitride layers and structures have been studied by photoluminescence (PL) spectroscopy at room and low temperatures. Temperature-dependent PL measurements under low excitation exhibit “S”-shaped behaviour of the emission peak energy due to the carrier localization at low temperatures ( $T < 50\text{K}$ ). The localization energy has been assessed to be 27 meV. Single-junction p-i-n solar cells with conversion efficiency above 4 % have been realized based on compensated dilute nitride i-GaAsSbN layer. The obtained results highlight the potential of the LPE as a prospective method for the fabrication of photovoltaic devices based on dilute nitrides.

**Acknowledgements:** This work was supported by the European Regional Development Fund within the Operational Program “Science and Education for Smart Growth 2014 - 2020” under the Project CoE “National centre of mechatronics and clean technologies“ BG05M2OP001-1.001-0008 and by the Bulgarian Ministry of Education and Science under the National Research Program E+: Low Carbon Energy for the Transport and Households, grant agreement D01-214/2018.

## Effects of laser power and excitation wavelength on the Raman spectra of nanostructured materials

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This study provides an overview of the influence of laser irradiation power on nanostructured samples, as well as the effects of excitation wavelength selection on the Raman spectra of these materials, especially under the resonant conditions. After a brief introduction to the Raman scattering basics, a method for estimation of temperature change by measuring the ratio of the Anti-Stokes to Stokes intensities of the  $E_g$  phonon mode of anatase  $\text{TiO}_2$  nanopowder is demonstrated. Huge broadening and blue-shift of the  $E_g$  mode observed under intensive laser illumination are attributed to laser-induced heating effects [1]. The micro-Raman systems use microscope objectives to focus the laser onto the sample, which drastically increases the spatial resolution, but focused laser beam may heat and alter the studied material. Although laser heating effects are usually reversible, material nanostructure could be seriously modified after intensive irradiation. The analysis of the various parameters affecting laser-induced thermal changes during micro-Raman measurements is presented, providing insight into adjusting the laser power in order to find a compromise between the Raman signal intensity and the risk of thermal change. It is shown how increasing laser power can lead to a drastic change in Raman spectra in the case of carbon- $\text{TiO}_2$  nanocomposites [2], but also to a change in the composition of nanolayers based on II-VI compounds. The choice of laser excitation wavelength can also significantly affect the Raman spectra of some nanomaterials depending on their thermodynamic and optical properties. Thus, a change of the laser line can lead to a change in the laser-induced heating or to a decrease of the background signal due to luminescence often present in nanomaterials. Here, special attention is paid to variation in the Raman spectra due to resonance enhancement of Raman scattering. The analysis of the Raman spectra of zinc-selenide based thin films under resonant condition has shown that a specific behavior of longitudinal optical phonon modes in these spectra could be related to size-induced variation of the optical band gap of investigated nanostructures [3,4]. The Phonon confinement model, modified to simulate the Raman spectra excited by different laser lines, both in non-resonant and near-resonant conditions, is also presented [4].

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**ABSTRACTS**  
**ORAL PRESENTATIONS**



## Improving the Photocatalytic and Sensing Properties of Sol-Gel ZnO Thin Films by Modifying the Way of Preparation

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The surface morphology and structure of zinc oxide thin films play a key role in various applications of this multifunctional material, in particular for important application of ZnO in chemical sensing and photocatalysis. Chemical sensors are applied for environmental pollutant determination, while the photocatalysis is a clean technology for the degradation of various toxic organic materials used in many industries. Various ways have been developed to enhance ZnO chemical sensitivity and photocatalytic activity under UV and visible light illumination, such as doping, "green synthesis" of nanoparticles from bio-organisms, etc.

In this study, undoped sol-gel ZnO single layers were prepared by applying spin coating technique and a modified drying procedure. It consists of two-steps - hot air drying (HD) ( $T_h=90-95\text{ }^\circ\text{C}$ ), as first step and conventional furnace treatment (CT) at  $140^\circ\text{C}$ . as second step. For comparison a second group of films was produced by applying only standard CT at  $140^\circ\text{C}$ . A part of the films from both groups were further annealed at  $400^\circ\text{C}$ . It has been shown that hot air drying has significant influence on the films properties. It gives assistance to the effusion of organic remains and results in a better film crystallinity, strongly affects the films surface morphology, reduces the internal stress and defect density in the as-prepared HD-films when compared with the CT-films [1]. Photocatalytic activity for the degradation of Malachite Green dye and ethanol sensing properties were explored. The investigation of the effect of the drying procedure on the photocatalytic reaction rate have shown that the HD-films demonstrate significantly higher photocatalytic activity and better stability (up to 6 photocatalytic cycles) than the CT-films under both ultraviolet and visible light illumination. Good response to ethanol vapours has been observed at room temperature.

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**Acknowledgement:** DN and VD acknowledge the financial support provided by the European Regional Development Fund within the OP "Science and Education for Smart Growth 2014 - 2020", project No BG05M2OP001-1.001-0008.

## Composite catalysts on interactive oxide support for alkaline water electrolysis

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A The new trend in the field of hydrogen production by water electrolysis is the development of electrochemical cells, operating with a polymer anion conducting membrane (AEMEC), which are expected to combine the advantages of alkaline electrolyzers, working with liquid electrolyte (use of cheaper non-precious metal catalysts) with those of the systems using proton conductive polymer electrolyte membrane (PEMEC) - high efficiency, environmental friendliness, compatibility with the renewable energy sources. The recent research is focused on the preparation and study of composite nanosized materials based on cobalt and nickel deposited as nanoparticles on non-stoichiometric mixture of titanium oxides, their physicochemical characterization and investigation of the Me/support interactions on the electrocatalytic activity toward the classical alkaline water electrolysis partial electrode reactions. The common electrochemical techniques of cyclic voltammetry and polarization curves are used to obtain information about the proceeding changes in the oxidation state of the catalysts on the electrochemically active surface, as well as to determine the potentials of hydrogen and oxygen offset and the corresponding current densities. Selected catalysts are integrated in membrane electrode assemblies with anion exchange polymer membranes and tested in a custom made AEMWE single cells. It is found that the composite catalysts under study facilitate essentially the partial electrode reactions compared to the unsupported metal nanoparticles. The performed long-term potentiostatic tests proved the stability of the catalysts with time and ensured good service durability. The results obtained allow considering these complex structures as promising catalysts for hydrogen production via alkaline water electrolysis.

**Acknowledgements:** The authors kindly acknowledge the financial support of project №BG05M2OP001-1.002-0014 „Center of competence HITMOBIL - Technologies and systems for generation, storage and consumption of clean energy”, funded by operational Programme “Science and Education for Smart Growth”.

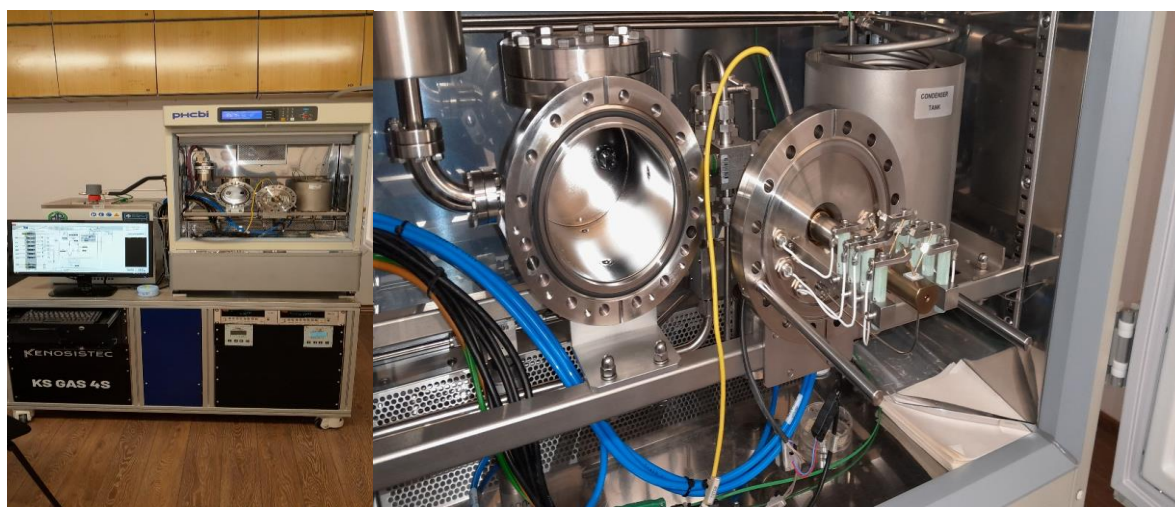
## Gas sensor test equipment Kenosistec KGAS4S. How does it work and areas of application

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The investigations of various resistive thin films and bulk structures, like oxides, chalcogenides, etc. are very important for chemical gas sensor application. The Kenosistec gas sensor testing system allows testing of samples by simulating real environment in a small volume. The change in the resistivity of structures and materials is measured in dependence on environment parameters, such as: humidity in the range of 10÷90%, temperature from 20 to 400°C, gas composition and concentration in the range of 1 to 5000 ppm. The system is equipped with 6 gas lines for feeding different gases into the measurement vacuum chamber under controlled humidity, temperature and concentration. Currently the testing system operates with CO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> gases with different composition and concentration. The chamber construction allows applying of additional optical stimulation of the sensors with visible and UV light. The measurement setup can also test and calibrate unbonded/unpackaged sensor devices.



**Figure 1:** Gas sensor test equipment Kenosistec KGAS4S.

**Acknowledgements:** The Kenosistec gas sensor system is purchased with the financial support provided by the European Regional Development Fund within the OP “Science and Education for Smart Growth 2014 -2020”, project No BG05M20P001-1.001-0008.

## Compression of neutral particles by an optical lens

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Ultra-short optical pulses can be used for the confinement of neutral particles by an additional optical longitudinal force, connected with the Poynting vector and the influence of the magnetic field on their polarizability. Experimental and theoretical studies are presented on the confinement and translation of particles by a femtosecond laser pulse. It is found that the longitudinal polarization force admits potential character and is closely related and connected to the time derivative of Poynting's vector. The Poynting vector is connected also to the intensity of the electromagnetic field. On other hand, the intensity of a laser pulse can be manipulated by an optical lens, and thus, indirectly, the optical force can be increased or decreased or its direction to be changed. This in turn enables a unique possibility for the compression of neutral atoms, molecules, and particles into the focus of the lens. Following the relation between the Poynting vector and the intensity of the pulse, we have obtained an analytical expression of this force and potential of a linearly polarized Gaussian laser pulse passing through a thin optical lens. Under the investigation, it is demonstrated that the propagation direction of the particles strongly depends on the particle sizes. Here, we reported on an experimental study of neutral particle confinement in the focus of femtosecond laser pulses and further confirmed by a theoretical investigation. The findings demonstrate an innovative approach to the compression and confinement of neutral particles within the focal plane of a lens and their further manipulation. Feasible applications could be in the field of cold nuclear fusion and cooling of light-neutral atoms and molecules.

### Acknowledgments

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## **Morphology control and enhanced sensitivity of thin film semiconductor oxides-based gas sensors: a fractal analysis study**

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The sensitivity of the sensors, along with their selectivity and fast response is one of their main characteristics. In addition to phase, the morphology of sensing materials, including shape, size, and orientation, plays a crucial role in gas sensing performance. One of the main strategies for improving the sensitivity of semiconductor oxide-based sensors is the morphology control. Nevertheless, the relation between the morphology of semiconducting oxide and the gas-sensing performance of the sensor using them are not clearly established yet. The high mean square surface roughness (RMS) value is not an unambiguous prerequisite for increasing sensor capabilities. Therefore, the understanding of favorable morphologies and the parameters of the microstructure at the interaction with gases are important for further improvement of gas sensors.

This study is seeking correlations between surface properties and gas sensing properties and will include investigation of morphology and surface roughness of sol-gel prepared ZnO thin films and thin films consisting of TiO<sub>2</sub> nanotubes of different geometrical parameters obtained by anodizing Ti, both designed for application as sensors for ethanol at room temperature. Attention was paid to the ability to control the topography of the films and the size of nanocrystallites and nanotubes by controlling the experimental conditions during deposition, and subsequent modification by conventional or laser annealing. The surface morphology and topography of the synthesized samples were studied by atomic force microscopy (AFM). The experimental results are used to analyze the roughness and porosity of the layers, as well as the size and size distribution of nanocrystals/nanotubes. Fractal analysis was carried based on AFM data. Fractal dimension and surface topographical properties is calculated from statistical metric. The surface images of the ZnO samples which have been showed the best sensor sensitivity are thoroughly investigated. The fractal analysis results and the surface volume ratio are analyzed. The model created is applied to project the the optimal samples to be possessing better gas sensing capabilities for the upcoming sensor measurements of thin films of TiO<sub>2</sub> nanotubes.

### **Acknowledgements:**

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## Measurement of nonlinear optical characteristics of wide bandgap semiconductor AlN using modified femtosecond z-scan method

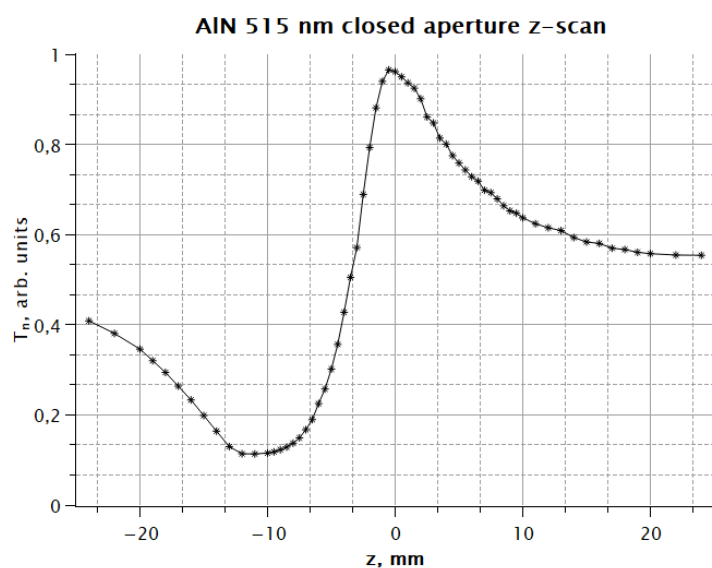
Mariam Shehadi<sup>1\*</sup>, Stefan Karatodorov<sup>1</sup>, Lyubomir Stoychev<sup>1</sup>, Docho Tsankov<sup>2</sup>, Todor Petrov<sup>1,2</sup>

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Aluminum nitride (AlN) has gained a lot of attention in the field of optoelectronics as a third generation wide bandgap semiconductor thanks to its excellent properties. Specifically, its large bandgap of ~6.2 eV makes AlN a significant material for manufacturing devices functioning across wide spectral range (wavelengths from IR to UV and deep UV). Implementing AlN in optoelectronic applications, such as UV/DUV emitters, photodetectors and nonlinear optical devices<sup>[1]</sup>, strongly depends on the accurate knowledge and understanding of the optical characteristics of AlN. For this purpose, in this work we measure the refractive index  $n_2$  and multi-photon absorption coefficient  $\beta$  of AlN single crystal using modified femtosecond z-scan technique. The obtained results are discussed.



**Figure 1:** Z-scan transmittance measurement of AlN sample as a function of its displacement along z-axis, in closed aperture regime at  $\lambda=515$  nm.

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## Raman characterization of low-dimensional nanostructures and single crystals

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The subtle interplay of vibrational properties and electronic band structure of graphene, carbon nanotubes and nanotubes of transition-metal dichalcogenides creates interesting effects in their Raman spectra. Different types of Raman resonances in these nanostructures are reviewed. Special attention is given to the description of the double-resonance Raman effect – a phenomenon which enables sampling of phonons from the Brillouin zone periphery with Raman spectroscopy. The antenna effect in carbon and tungsten disulfide nanotubes is reviewed as a case of resonant scattering from strongly anisotropic objects and the anisotropy parameter is determined. We also show how differences in the symmetry properties of zone-center phonons in bulk single crystals can be used for their assignment and, in some cases, for confirmation of the crystal structure.

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## Characterization of graphene and ALD grown Al<sub>2</sub>O<sub>3</sub>/graphene heterostructure

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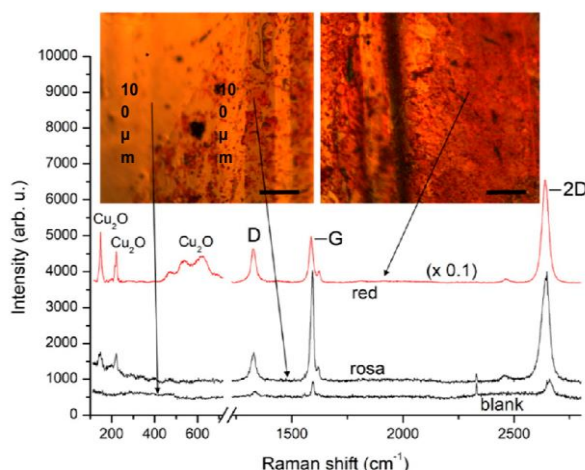
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Graphene films were grown by chemical vapor deposition on Cu foil. Graphene/Cu was covered by ALD grown Al<sub>2</sub>O<sub>3</sub> film, while graphene in the Al<sub>2</sub>O<sub>3</sub>/Graphene/Cu heterostructure retains its good quality. The obtained samples were characterized by Raman spectroscopy, ellipsometry and X-ray photoelectron spectroscopy. Effects of electropolishing on the quality and the Raman response of the grown graphene layers are studied by microtexture polarization analysis. The time-dependent changes in the samples are also investigated. We investigated single-layer graphene-coated Cu foils with respect to the Cu-graphene coupling and Cu oxidation to Cu<sub>2</sub>O as a way for its relaxation. The presence of Al<sub>2</sub>O<sub>3</sub> is manifested by a multiple enhancement of the Raman intensity of all graphene bands.



**Figure 1:** Micro-Raman spectra from different regions of a Gr/Cu foil several months after the CVD graphene growth process.

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Petar Rafailov, Petar Sveshtarov, Vladimir Mehandzhiev, Ivalina Avramova, Penka Terziyska, Minko Petrov, Boyko Katranchev, Haritun Naradikian, Stefan Boyadjiev, Csaba Cserhádi, Zoltan Erdélyi, Imre Szilágyi, “Growth and Characterization of Graphene Layers on Different Kinds of Copper Surfaces”, *Molecules* 27, 2022, 1789.

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## Thin Pt films as catalysts for electrochemical hydrogen compression

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One of the most technically challenging barriers in regard to broad industrial deployment of hydrogen energetics is the development of a safe, compact, and cost-effective hydrogen storage technology. The efficient storage requires pressurizing of hydrogen to medium or high pressure. The electrochemical hydrogen pump/compressor (EHP/C) is highly efficient, low-maintenance, and silent technology, which is considered as a potentially viable and cost-competitive alternative to the traditionally used mechanical piston compressors. The work presents a research on thin magnetron sputtered platinum (Pt) films deposited over commercial gas diffusion electrodes and applied to convert and pressurize hydrogen in an electrochemical hydrogen pump / compressor. The electrodes were integrated in a membrane electrode assembly with proton conductive membrane. Their electrocatalytic efficiency toward hydrogen oxidation and hydrogen evolution reactions were studied in a self-made laboratory test cell by steady state polarization curves and cell voltage measurements ( $U/j$  and  $U/P_{\text{diff}}$  characteristics). The achieved current density at cell voltage of 0.5 V, atmospheric pressure of the input hydrogen gas, and temperature of 60°C was more than 1.3 A.cm<sup>-2</sup>, while the registered increase of the cell voltage with the increasing pressure was only 0.05 mV.bar<sup>-1</sup>. The effects reveal an enhanced efficiency of both electrode reactions on the sputtered Pt compared to those observed on commercial E-TEK electrodes with four times higher platinum loading. The comparative data demonstrate not only a superior performance but also essential cost reduction of the electrochemical hydrogen conversion on the sputtered Pt films.

**Acknowledgements:** The authors kindly acknowledge the financial support of project № BG05M2OP001-1.002-0014 „Center of competence HITMOBIL - Technologies and systems for generation, storage and consumption of clean energy”, funded by Operational Programme “Science and Education for Smart Growth” 2014-2020, co-funded by the EU from European Regional Development Fund.

**ABSTRACTS**  
**POSTERS**

## The impact of physicochemical characteristics of carbon materials on the capacitive performance of symmetric supercapacitors with alkaline electrolyte

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Aqueous symmetric carbon supercapacitors have always been the focus of energy storage device research due to their low cost, intrinsic safety, and electrochemical stability. Due to the high ionic conductivity of aqueous electrolytes, they possess a much higher power density than non-aqueous organic electrolytes. The most commonly used electrodes are carbon-based porous materials with a high active surface and a porous structure, which are essential factors for achieving effective electrolyte accessibility and fast ion transport<sup>1,2</sup>.

In the present work, a symmetric supercapacitors consisting of electrodes with different activated carbons (ACs) and an alkaline electrolyte (6 M KOH) is reported. For comparison, supercapacitor cells with nonaqueous electrolyte (1 M LiBF<sub>4</sub> in ethylcarbonate/dimethylcarbonate (1:1)) were assembled with selected carbon materials. The activated carbons used are physicochemically characterized, and their main morphological and structural parameters such as particle size, surface area, porosity, etc. have been determined. Their capacitive characteristics were investigated by galvanostatic charge/discharge and long-term tests in a Swagelok electrochemical cell.

Symmetric supercapacitor cells demonstrate high discharge and stable capacitance as well as high efficiency of the charge-discharge process in alkaline electrolytes. Activated carbons with high specific surface area and microporosity exhibit the best performance in 6 M KOH.

In organic electrolytes, the investigated ACs show a lower capacitance than in alkaline electrolytes. The reasons for this result may be related to their morphology and the different (more complex) processes occurring in these mediums.

The obtained results indicate that the electrolyte conductivity and the adsorption of electrolyte ions in the electrode materials significantly affect the performance of supercapacitor systems. The important role of the morphology of the activated carbons for electrochemical characteristics of the symmetric supercapacitor was discussed.

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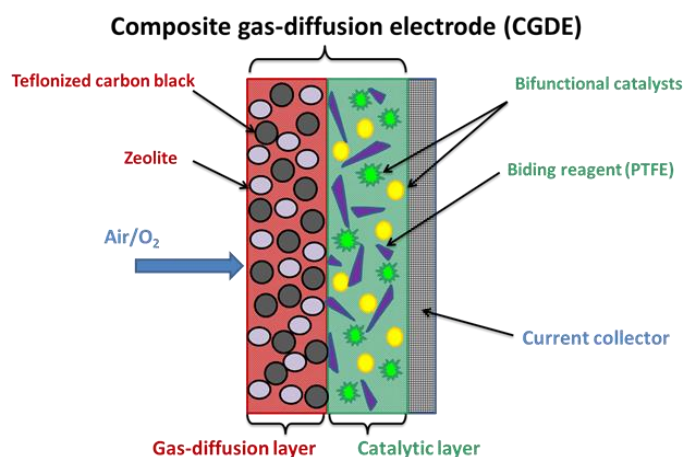
## Novel structure of composite gas-diffusion electrode (CGDE), containing zeolite for rechargeable metal hydride (MH)-air batteries

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The main advantages of rechargeable MH-air systems is their high capacity, low cost and environmental friendliness of the starting materials. The system contains two types of electrodes - the porous and hydrophobic GDE and MH electrode with high capacity. To improve oxygen diffusion in the GDE, various carbon and non-carbon materials with porous, layered and fibrous structures which possess gas diffusion channels were studied. One of the possible structures that meets these conditions is natural zeolites. By partially replacing the teflonized carbon black in the gas-diffusion layer (GDL) with zeolite, the necessary hydrophobicity was achieved, while maintaining the high gas permeability of the zeolite material. In the preliminary durability tests of innovative CGDE a high mechanical, chemical and electrochemical stability (more than 750 cycles) was observed in comparison to the carbon-based GDE.



**Figure 1:** Schematic of CGDE

**Acknowledgements:** The authors kindly acknowledge the financial support of project № BG05M2OP001-1.002-0014 „Center of competence HITMOBIL - Technologies and systems for generation, storage and consumption of clean energy”, funded by Operational Programme “Science and Education For Smart Growth” 2014-2020, co-funded by the EU from European Regional Development Fund.

The equipment used is provided with the assistance of the Bulgarian Ministry of Education and Science under the National Roadmap for Research Infrastructure 2017-2023 approved by DCM No354/29.08.2017, “Energy storage and hydrogen energetics” (ESHER)

## The effects of ultrafast laser pulses on the properties of advanced medical-grade PDMS polymer

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The effects of the femtosecond laser pulse irradiation on the modification and activation effects of medical-grade polydimethylsiloxane (PDMS) polymer are investigated. The motivation of the research is based on the continuous interest and variety of applications of the PDMS material in medicine and implantable neural interface devices. The PDMS is the preferred material due to its exceptional properties such as high biocompatibility and biostability, mechanical flexibility and stability, optical transparency from UV to near IR spectral region, and cost-effectiveness. The experimental investigation is performed by a femtosecond laser system with a pulse duration of 35 fs operating at a repetition rate of 1 kHz. Consistent sets of measurements are performed to analyse and characterize the effect of the laser beam parameters on the optical absorption, and surface morphology concerning the laser-treated zones. The PDMS's morphology and optical properties are investigated to activate its surface for successful metallization of the modified tracks. The reported findings and observations specify favorable results of implementing the ultrafast laser-based method for micro- or nano-processing optically transparent biopolymers for interface devices in bioengineering technologies such as neural implants and interface applications. The authors aim in future research to perform the investigation concerning the structural properties of the medical grade PDMS and extend the study to the NIR spectral region.

### Acknowledgments

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## SPR sensors biochips based on protected silver/copper layers

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A major problem for surface plasmon resonance (SPR) biosensors is the preservation of the biological activity of the immobilized ligand molecules. Basically, the plasmon resonance is excited in a gold metal layer, but it is known that in contact with this surface, biomolecules lose about 90% of their bioactivity. The situation is roughly the same with other metals. However, silver and copper possesses a sharp SPR-dip, which is desirable because it usually results in a better signal-to-noise ratio. The sharp dip depends on the ratio  $W=|\epsilon'|/|\epsilon''|$  between the real and imaginary parts of the material's complex refractive index  $\epsilon=\epsilon'+\epsilon''$ . Silver ( $W=37.96$ ), copper ( $W=20.38$ ), and gold ( $W=7.33$ ) give the highest ratios; however, only gold is used in practical applications as the chemical inertness of thin silver and copper layers is poor, causing them to corrode quickly in aqueous buffers containing oxygen and salt.

The question arises whether the advantage of silver and copper in terms of the highest  $W$  ratio does not give the possibility of applying a shielding coating, which solves the problem of preserving bioactivity and protects from corrosion? Herein, we report the results of our study. We studied the plasmon resonance in diffraction gratings coated with a layer of silver and copper about 120 nm thick. The parameters of the plasmon resonance were compared with that obtained after deposition on Ag/Cu layers a protective layer of ITO or MgF. The protective layers strongly change the resonances - shifts them to longer wavelengths and increase the FWHM. This effect depends on the technological conditions of layer deposition. The optimal conditions were determined and for them the dependences on FWHM as a function of the protective layer thickness were established. We found that ITO protective layer is more effective.

Although the protection of the silver/copper layer is at the expense of FWHM, conditions can be found where achieved FWHM is narrower than that of in a gold. This shows the feasibility of SPR biosensors, where the resonance is realized in silver or copper metal layers.

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## Synthesis and characterization of TiO<sub>2</sub>/WO<sub>3</sub> nanocomposites with enhanced photocatalytic activity

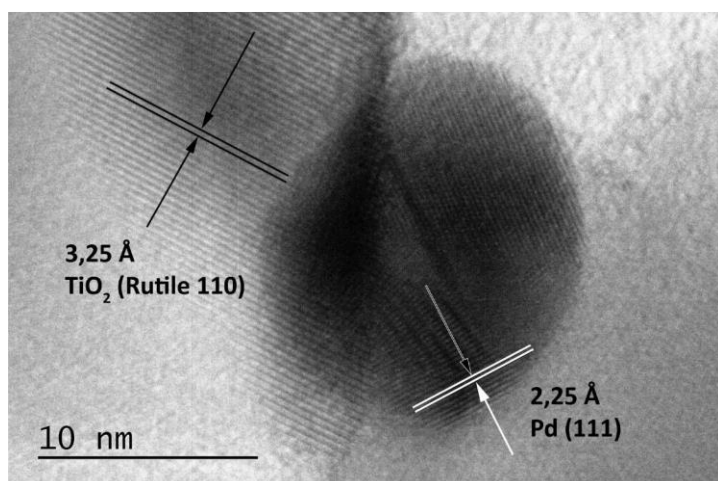
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The most promising semiconductor oxide materials, titanium dioxide has excellent photocatalytic activity and stability, but is only active under ultraviolet light irradiation because of its wide band gap. Modifying TiO<sub>2</sub> in various ways changes the mechanism and kinetics under UV irradiation but also introduces visible light activity that is absent with pure TiO<sub>2</sub>. The aim of the present study was to synthesize photocatalysts on the basis of TiO<sub>2</sub>, combining it with WO<sub>3</sub> and noble metals. The nanocomposites were synthesized by extractive-pyrolytic method by loading 4 wt.% WO<sub>3</sub> and 1 wt.% of the active metal having particles size varying from 5 to 30 nm. The XRD, XPS, TEM and BET methods were employed for their structural and chemical characterization.



**Figure 1.** HRTEM image of TiO<sub>2</sub>/WO<sub>3</sub>/Pd catalyst sample.

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## Raman spectroscopic evidence for multiphase composition in copper tin sulfides

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The growing demands on energy have incited research and development of novel multifunctional materials, which must meet requirements like abundant raw materials, innocuousness, inexpensiveness, high performance, etc. Copper tin chalcogenides, such as  $\text{Cu}_2\text{SnS}_3$  and  $\text{Cu}_2\text{SnSe}_3$ , are candidates to meet these requirements.  $\text{Cu}_2\text{SnS}_3$  in particular attracts much interests due to outstanding characteristics like direct band gap 1 eV, high absorption coefficient ( $10^4 \text{ cm}^{-1}$ ) and good electrical properties [1].

However, the formation of CTS single-phase material faces a couple of obstacles. According to the phase diagram of  $\text{Cu}_2\text{S-SnS}_2$ , there are few compounds ( $\text{Cu}_2\text{SnS}_3$ ,  $\text{Cu}_2\text{Sn}_3\text{S}_7$ ,  $\text{Cu}_3\text{SnS}_4$  and  $\text{Cu}_4\text{SnS}_4$ ) that are stable and coexist at room temperature [2]. Furthermore, the correct identification of the presented crystallographic phases in the Cu-Sn-S (CTS) system is even harder due to similarity in unit cells parameters and diffraction positions, which make the unequivocal differentiation of a distinct crystal structure quite tough task. Raman scattering is very powerful and usable in this particular case, since it is very sensitive and able to catch small deviations from the crystal parameters – atom position, angle, bond strength.

The present study aims to explore the physicochemical properties and electrochemical storage abilities of copper-tin-sulfides system. The Raman scattering and X-ray diffraction analyses indicate presence of two CTS compositions ( $\text{Cu}_2\text{SnS}_3$  and  $\text{Cu}_3\text{SnS}_4$ ) with tetragonal symmetry and non-stoichiometric  $\text{Cu}_{1.95}\text{S}$ . The composite was tested electrochemically in lithium half-cell configuration using cyclic voltammetry and galvanostatic test.

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## **Kinetics, equilibrium and thermodynamics of Congo red removal by cationized materials based on agricultural waste**

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Many industries such as textiles, food, leather, paper, printing, pharmaceutical, cosmetics, etc. generate considerable amounts of dye-bearing effluents during their production processes. Most of these dyes represent serious problems to the ecological system as they are considered toxic and have carcinogenic properties. Therefore, dyes removal is an important and challenging area in wastewater treatment. Congo red (CR) is a synthetic anionic diazo dye. It is a significant hazard to aquatic living organisms and a human carcinogen.

The present study deals with the removal efficiency regarding Congo red dye of novel cellulose biosorbents prepared from agricultural waste products. The rice and einkorn husks were used as raw materials to extract and separate the cellulose by alkali and bleaching treatment. The cellulose materials were modified with N,N-dimethyl-1-octadecylamine to prepare cationized sorbents. Instrumental methods such as XRD, DTA, FTIR, SEM as well as low-temperature nitrogen adsorption were used for their characterization. The removal of lignin and hemicellulose from the plant matrix leads to a change in the surface morphology of the samples; their phase composition; surface functional groups and porous structure. The characterization of cationized materials shows that the quaternary ammonium group was successfully grafted onto cellulose structures. The survey mainly focused on the effect of process parameters on the adsorption capacity of investigated materials, including initial Congo red concentrations, solution pH and temperature. Equilibrium data were fitted to pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models and linear Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. The adsorption process was well described by pseudo-second-order and Langmuir models. The material based on einkorn husks demonstrate slightly higher CR removal performance with an adsorption capacity of 121.51 mg/g, according to the Langmuir model. The negative values of change in Gibbs free energy and enthalpy change indicate that adsorption of CR onto studied biomaterials is spontaneous and exothermic with a negative entropic change. Based on the experimental results, it can be concluded that novel cationized cellulose materials can be used as potential adsorbents for the effective removal of CR from contaminated aqueous solutions. 0.1M NaOH solution is a suitable eluting agent for the regeneration of both biosorbents. The obtained results reveal that renewable agriculture wastes can be successfully processed into products with added value and applicability in protecting the environment from hazardous pollutants.

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## Optical spectroscopy of photochromic fluorescent spirooxazines sensitive to metal ions

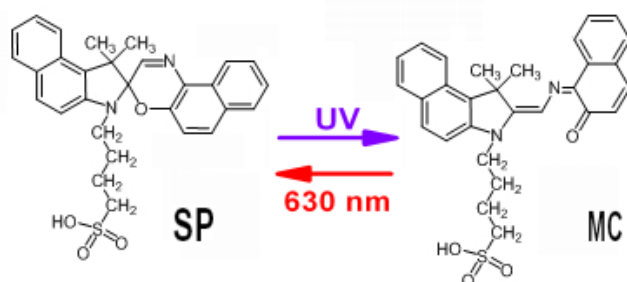
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The fluorescence properties and photoswitching behavior of newly synthesized spirooxazine derivatives are investigated in dilute solutions ( $10^{-4}$  –  $10^{-5}$  M) under photo-excitation with continuous light at low intensity ( $1$  –  $10$  mW/cm<sup>2</sup>) in the UV spectral range, as well as by illumination with light in the red region of the spectrum. In the first case, photoinduced molecular isomerization from spiro-form (SP) to merocyanine-form (MC) takes place, in the second – the reverse photoinduced process (Figure 1). The photoinduced fluorescence emission from the examined solutions is in the green spectral range. The interaction of spirooxazines with Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, or Pb<sup>2+</sup> ions leads to the formation of merocyanine molecular forms and metal-organic coordination complexes that absorb light in the visible spectral region. Thus, the change in the intensity of the absorption band around 630 nm can be used for optical detection of the presence of metal ions in the solutions. By that, the spectra of the photoswitchable fluorescence of these photochromic compounds in solutions can perform an auxiliary registration function. Determination of the photo-physical characteristics of the studied spirooxazine compounds are useful for elucidating the photo-chemical mechanism of the photo-transformations of the involved molecular conformers, which can be used in various photo-controllable applications. Furthermore, the molecular conformers of the spirooxazines and their complexes with metal ions were characterized optically in order to optimize the electronic and stereochemical structure of the synthesized spirooxazine compounds, and accordingly – to optimize their synthesis. The results show that by specific structural modification of the investigated spirooxazine derivatives, their fluorescence efficiency, the photo-switching behavior, as well as their sensing response to metal ions, can be significantly improved.



**Figure 1:** Spirooxazine isomers and set-up for optical spectroscopy of their dilute solutions.

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## Highly efficient catalyst applicable in electrochemical hydrogen pump/compressor

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The electrochemical hydrogen pump is an efficient device for hydrogen cleaning and compression which offers several advantages overall the mechanical compressors such as absence of moving parts, no need of vacuuming and periodical lubrication, possibility to operate at higher differential pressure, etc. However, the technology is still a challenge due to the need of high catalytic loadings of Pt based catalysts for both partial reactions – hydrogen evolution and hydrogen reduction (HER and HOR, respectively), which makes the system rather expensive. This work presents the synthesis and performance of bi-metallic (Pt/Pd) and (Pt/Ir) catalysts integrated in cathode and anode of a recently developed laboratory electrochemical hydrogen pump/compressor (EHC), operating with proton conductive membrane Nafion 117. The electrode construction is significantly optimized compared to the state-of-the-art cells. The initial laboratory tests performed demonstrated that the architecture of the electrodes ensures high intensity of both HOR and HER, and a cell energy efficiency of 85% as well as a possibility to operate with identical gas compression rate at different input hydrogen pressure.

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## Physicochemical and electrocatalytic properties of non-stoichiometric Ba<sub>2</sub>Sr<sub>2</sub>La<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> perovskites

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The global climate change and ever-growing energy demand that the society has been facing in recent years impose the research and development of advanced technologies and devices for energy production and storage. These devices must meet a number of requirements: less toxicity, lower cost, abundance, environmental friendliness and improved efficiency. Metal-air batteries are considered to be a good candidate for storage of energy as they have many advantages over other types of batteries (lithium-ion, metal hydride and lead-acid) in particular the use of oxygen directly from the air, higher specific energy, the abundance and non-toxic nature of some anode materials (Zn, Al, Mg, Fe, Ca, etc.).

This study explored the effect of the pretreatment milling media (deionized water (BLTOS-H) and isopropanol (BLTOS-i)) on the chemical and phase composition, surface characteristics and catalytic activity of non-stoichiometric Ba<sub>2</sub>Sr<sub>2</sub>La<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> perovskites. The IR spectroscopy and X-Ray Diffraction indicate a difference in the structure and phase composition of the two samples. Ba<sup>2+</sup>, La<sup>3+</sup> enrichment and Sr<sup>2+</sup>-depletion was observed on materials' surface by X-Ray Photoelectron Spectroscopy. BLTOS-i shows higher specific surface area (SSA) and pore volume compared to BLTOS-H.

The prepared materials were deposited on the surface of an air-gas diffusion electrode (AGDE) in order to assess the catalytic activity regarding oxygen reduction reaction (ORR) in metal-air electrochemical system. The tests were conducted in three-electrode experimental cell using nontoxic NaCl electrolyte, stainless steel plate as the counter electrode and Ag/AgCl as the reference electrode. BLTOS-H and BLTOS-i were compared to AGDEs containing 5 wt.% Pt or 4 wt.% Ag deposited on the surface of activated carbon. BLTOS-i exhibits highest electrochemical performance among all tested samples over the entire current range, while BLTOS-H presents similar polarization to platinum (5 wt.%) at current densities up to 10 mA cm<sup>-2</sup>.

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## Electrochemical properties of carbon xerogel-based supercapacitors using non-aqueous electrolytes

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Supercapacitors are energy storage devices that have attracted much attention because they are able to provide high power densities of up to 10 kW kg<sup>-1</sup> (unlike batteries) and have long lifetimes<sup>1</sup>. However, their main drawback is the inability to store high energy density, which has prompted research into new carbon electrode materials. When selecting them, it should be kept in mind that the efficiency of supercapacitors depends on both their porosity and their electrical conductivity, and the higher their microporosity, the higher the charge that can be stored<sup>2</sup>. The use of an organic electrolyte, which allows a much wider and stable potential window compared to aqueous one, is also a prerequisite for obtaining a high energy density devices<sup>3</sup>.

The present study aims to show the relationship between the surface chemistry of carbon xerogel and its electrochemical properties as an electrode material in symmetric supercapacitors with organic electrolytes.

Carbon xerogels were synthesized by polycondensation of resorcinol and formaldehyde followed by carbonization and activation. Their porous properties were modulated by changing the pH of the precursor solutions and characterized by N<sub>2</sub> adsorption-desorption isotherms, a helium pycnometer and a shell density analyzer. The obtained samples were characterized physiochemically by DTA/TGA, TEM, XRD, SEM analyses. The results show that the synthesized carbon xerogels are porous with a high specific surface area, which is a necessary condition for their good electrochemical performance as electrode materials in supercapacitors. With the resulting carbon xerogel and organic electrolytes (LiBF<sub>4</sub> EC:DMC 1:1 and 1-ethyl-3-methylimidazolium tetrafluoroborate), two-electrode symmetric supercapacitor cells were assembled and investigated by galvanostatic charge/discharge measurements and cyclic voltammetry to assess their lifetime stability and electrochemical performance. Specific capacitances, energy and power densities, Columbus efficiency and energy efficiency were also calculated. The highest stability is shown by the symmetric carbon xerogel supercapacitor in LiBF<sub>4</sub>/1-ethyl-3-methylimidazolium tetrafluoroborate electrolyte than in LiBF<sub>4</sub> electrolyte.

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## Nematic liquid crystals/polymer composites as ion conductors

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Nowadays, various kinds of advanced multifunctional composite materials from polymers and liquid crystals have been developed and thoroughly investigated due to their important properties. Such soft or soft-solid materials, in particular, flexible and stretchable composites of polymers and nematic liquid crystals (NLCs), have found a wide variety of applications, e.g., in flexible displays, flexible organic electronics, sensorics and mechatronics, as well as for rechargeable flexible batteries and wearing electronics. The interest in such complex ion-conducting plastic materials rose rapidly since they have been proposed as polymer electrolytes for energy storage applications [1]. Interesting results have been reported for composites synthesized from ion-conducting polymer poly(ethylene oxide) (PEO) and the room-temperature NLCs with the commercial name E8 that showed the possibility of producing flexible thin films (50 – 200  $\mu\text{m}$  thickness) with enhanced ionic conductivity and improved dielectric properties [2]. In these cases, a synergistic effect was achieved due to electrostatic interaction (attraction) and intermolecular coupling of the molecules of NLCs (being electric dipoles) to the polar functional groups in the structural units of the polymer chains. Suitable example to illustrate the intermolecular force-induced coupling of NLC molecules to the molecular structure of PEO is the salt-complexed ion-polymer coupled system PEO/E8/NaIO<sub>4</sub> (polymer ion-conducting electrolyte) containing small amount of the salt sodium metaperiodate (NaIO<sub>4</sub>) as a dopant of Na<sup>+</sup> ions. The dipolar (dipole-dipole) interaction between PEO and E8 was confirmed by analyses of results obtained by UV-Vis absorption spectroscopy, vibrational optical spectroscopy, complex electrical impedance and dielectric spectroscopy, as well as by analysis of thermal behaviors of these composites [2].

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## Electrochemical investigation of carbon based gas diffusion electrodes (GDEs) for rechargeable metal hydride (MH)-air battery

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Rechargeable MH-air batteries are extremely promising because they combine the advantages of nickel-MH batteries on one hand and the practically unlimited capacity of the GDE on the other hand. In the present study teflonized carbon black (Vulcan XC-72 R) was used for producing a mechanically, chemically and electrochemically stable gas diffusion layer. A mixture of different commercial catalysts such as: (Ag, Ag+Co<sub>3</sub>O<sub>4</sub>, Ag+ $\gamma$ -MnO<sub>2</sub> and Ag+NiCo<sub>2</sub>O<sub>4</sub>) were used to build the catalytic layer (CL) of the GDE. The electrochemical properties of several GDEs with different CL were investigated using polarization (fig.1) and charge/discharge durability tests in half cell configuration in 6M KOH. The charge/discharge time was 45/30 min, respectively. Long-term tests of the GDEs showed very good stability of over 300-500 cycles. The GDEs were also tested in a configuration with MH electrodes (rechargeable battery) and that stability was confirmed.

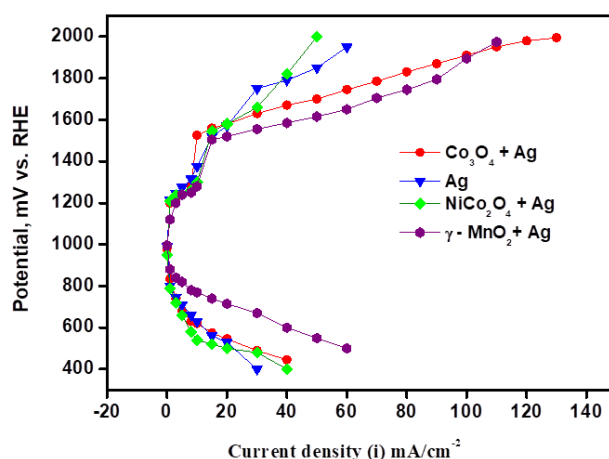


Figure 1: Polarization curve of GDEs with different CL

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The equipment used is provided with the assistance of the Bulgarian Ministry of Education and Science under the National Roadmap for Research Infrastructure 2017-2023 approved by DCM No354/29.08.2017, “Energy storage and hydrogen energetics” (ESHER)

## Effect of the conductive additives on the capacitive performance of symmetric supercapacitors based on activated carbon in alkaline electrolyte

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Symmetrical supercapacitors are now attracting both research and technological interest because they provide excellent stability over many cycles. The function of supercapacitors is based on the reversible adsorption of electrolyte ions in the electrode materials. Therefore, the appropriate selection of electrode materials determines the supercapacitors performance.

In the last decade, special attention has been paid to nanostructured carbon materials produced from renewable bioresources, which have great potential in rechargeable energy storage systems. Activated carbon is widely used as an electrode material due to its high specific surface area, but this results in poor electrode conductivity. It can be improved by adding various conductive additives, which must be chemically stable in the electrolyte solution and must be uniformly distributed in the volume of the electrode mass.

In the present work, activated carbon (YP-50F) was used as the electrode material to assemble supercapacitor cells. Activated carbon is a commercial product kindly provided by Kuraray Europe GmbH and obtained from coconuts as raw material. Various conductive additives to the active mass, such as graphite, graphene oxide and acetylene black, have been investigated for their influence on the capacitive performances of symmetrical supercapacitors.

*Electrochemical tests:* The supercapacitor cell contains two identical electrodes from activated carbon (80%), conductive additive (10%) and binder (10%). Polytetrafluoroethylene (PTFE) as binder was previously added to activated carbon using a standardized procedure. The formed sheet electrodes were dried at 120 °C for 6 hours and pressed under 20 MPa pressure. The electrodes were soaked in the electrolyte (6M KOH) under vacuum and then mounted in a coin-cell with Viledon 700/18F separator and filled with electrolyte. The supercapacitors were tested by different electrochemical methods such as cyclic voltammetry at different scan rates from 10 to 50 mVs<sup>-1</sup> in the voltage range of 0.05–1.2V, galvanostatic charge/discharge measurements and long-term durability tests.

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## Materials, structure, function and possibilities of AEM-URFCs

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Anion exchange membrane unitized regenerative fuel cells (AEM-URFCs) can reversibly operate as both a fuel cell and an electrolyzer. They are a promising technology for energy storage and electricity production due to their less corrosive operating environment and possible use of low-cost membranes, inexpensive component materials, and PGM-free electrocatalysts while offering competitive performance.

The main active element of URFC is the membrane electrode assembly (MEA), which consists of two gas diffusion electrodes located on both sides of a polymer electrolyte membrane (in the case of anionexchange(AEM)). Each constituent part of the MEA, affects the performance, efficiency and sustainability of the the entire system.

This work reviews the current state of art of this promising technology and identifies the main technical challenges to overcome to make the AEM-URFC system more technologically and economically viable. It aims as well to prove the concept of operation of a laboratory AEM-URFC.

An MEA of AEM-URFC was fabricated with commercial gas diffusion electrodes ETEK (0.4 mg.cm<sup>-2</sup> Pt/C, both cathode and anode) and a laboratory-synthesized anion-conducting membrane of para-polybenzimidazole doped with 50% KOH (p-PBI). The obtained MEA was studied in a laboratory cell in two modes of operation - electrolysis and fuel cell, at room temperature, and has it has showed stable working characteristics.

The work of the AEM-URFC was also modeled using the theoretical thermodynamic functions and electrochemical equations by means of free Scilab 6.0 software, allowing the calculation of the U/j characteristics as well as parameters such as reversible potential, activation and ohmic losses of the electrochemical process.

From the obtained results, we conclude that the assembled cell is suitable for operation both in electrolysis and in fuel cell mode, and can subsequently be used to study newly synthesized catalysts/electrodes for AEM-URFC operation.

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## Europium doped germanate glass-ceramics containing $\text{Ca}_5\text{Ge}_3\text{O}_{11}$ as a main phase for potential red phosphor application

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Europium doped glass-ceramics from the oxide system  $\text{CaO-GeO}_2\text{-Li}_2\text{O-B}_2\text{O}_3$  were prepared by thermal treatment of the glasses with composition 40:43:5:12 mass% and dopant concentration 4at% calculated relative to the concentration of the  $\text{Ca}^{2+}$ . The parent glasses were heated between 570 and 630°C with a step of 10°C and holding at each temperature for 2 hours. XRD patterns confirm the crystallization of  $\text{Ca}_5\text{Ge}_3\text{O}_{11}$  as a main phase and  $\text{Li}_2\text{GeO}_3$  as a second phase. The crystal part in the obtained samples varies between 20 and 60%. The mean particle size determined from TEM images varies between 2 and 10 nm.

Excitation and emission spectra of the glass-ceramics possess the characteristic peaks of the  $\text{Eu}^{3+}$  ion. The highest peak in excitation spectra is located at 393 nm caused by  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  transition. The emission spectra include  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_{0, 1, 2, 3, 4}$  transitions peaked at 579 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ ), 592 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ), 612 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ), 652 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ ) and 702 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ ). The highest peak is ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ) transition located at 612 nm, meaning that the active ion is not located in an inversion center. These spectra are identical with the spectra of  $\text{Eu}^{3+}$  doped  $\text{Ca}_5\text{Ge}_3\text{O}_{11}$  compound. The highest luminescent intensity is observed for the sample thermal treated at 600°C. After thermal treatment at higher temperatures no significant change in luminescence intensity was observed.

Chromaticity coordinates of the obtained glass-ceramics are located in the red region of the color space with small variations around the values (0.65, 0.35). The obtained results show that the investigated glass-ceramics could be used as red phosphors.

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## Structural characterizations of 2D Tungsten Diselenide

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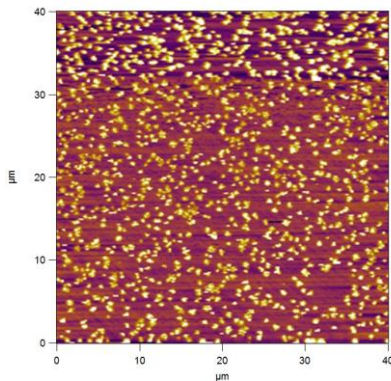
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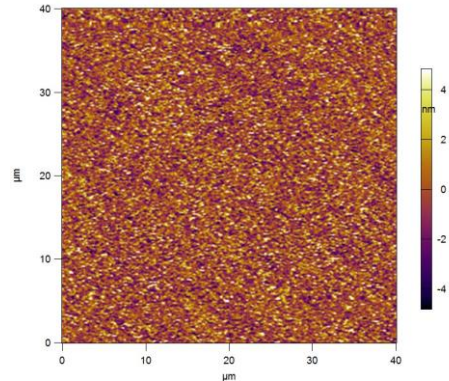
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Transition metal dichalcogenides (TMDCs) are a large class of inorganic layered materials composed of transition metals (such as molybdenum, tungsten, niobium, etc.) sandwiched between two layers of chalcogen (sulfur, selenium or tellurium) atoms. Tungsten diselenide (WSe<sub>2</sub>) is a semiconducting example of those materials. In single-layer form, WSe<sub>2</sub> shows ambipolarity and direct bandgap, already used to realize electrically tunable PN junctions, demonstrating its potential for digital electronics and solar cell applications. Yet its industrial synthesis remains a challenge.

Here, we report the synthesis details of WSe<sub>2</sub> using an atmospheric pressure thermally assisted conversion (TAC) method, where the tungsten (W) layers were pre-deposited by a magnetron sputtering system on fused silica substrates. Atomic force microscopy (AFM) mapping predominantly revealed the formation of isolated flakes with different shapes, mainly concentrated near the substrate's edges, which tended to form clusters and to further overlap to continuous layers, moving to the central part of the substrates. Raman spectroscopy confirmed the existence of atomically thin flakes and 2H-WSe<sub>2</sub> continuous layers.



**Figure 1:** AFM image of WSe<sub>2</sub> (edge)



**Figure 1:** AFM image of WSe<sub>2</sub> (center)

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V. M., N. M., T. B. and P. R. acknowledge the financial support by the European Regional Development Fund within the Operational Programme ‘Science and Education for Smart Growth 2014–2020’ under the Project CoE ‘National Center of Mechatronics and Clean Technologies’ BG05M2OP001-1.001-0008-C01. Research equipment of Distributed Research Infrastructure INFRAMAT, part of the Bulgarian National Roadmap for Research Infrastructures, supported by the Bulgarian Ministry of Education and Science was used in these investigations.

## Microwave-assisted synthesis of Phosphorus containing Composites as Functional Electrocatalytic Materials

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Here we report the optimization of microwave-assisted synthesis of phosphorus containing composites base on clinoptilolite with Cellulose phosphate for applications at electrolysis of sea water and purification of polluted waters from organic contaminants.

Microwave irradiation conditions, such as irradiation power and time, and the ratio of starting reagents were optimized. We have obtained the best results with a ratio natural Clinoptilolite:P-containing materials 1:3 by weight.

Obtained new synthesized a material has been characterized by physicochemical methods like: EDX, SEM, BET, and XRD. Novel electrode materials are studied with electrochemical techniques.

Our studies show that microwave-assisted synthesis is an appropriate method to obtaining of these composites. The physicochemical analysis shown successful incorporation of phosphorus compound on clinoptilolite. The obtained phosphorus containing functional materials have electrochemical activity and can be used in the purification of water contained organic contaminants.

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## Structural Characterization of $Ce_{1-x}Sm_xO_{2-x/2}$ Powders Prepared by Ionic Gelation and High Temperature Techniques

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Ceria-based materials and in particular those, doped with rare earth elements like Gd and Sm, have been intensively studied recently due to the wide area of their application, provided by their unique properties such as chemical and thermal stability and oxygen ion conductivity, which could be significantly improved by substitution of  $Ce^{4+}$  with different metal ions. This is why, they are a subject of extensive research from the point of view of their use as an electrolyte material in solid oxide fuel cells.

In the present work, we have prepared Sm - doped cerium oxides  $Ce_{1-x}Sm_xO_{2-x/2}$  by ionic gelation and solid state reaction approach. The influence of the preparation method on some physicochemical properties of the obtained final materials has been investigated and discussed. The samples obtained by ionic gelation were synthesized by gelling of initial solutions of sodium alginate and metal nitrates ( $Ce(NO_3)_3 \cdot H_2O$ ,  $Sm(NO_3)_3 \cdot H_2O$ ) and following thermal treatment of the gel at 500 °C. The synthesis of the second serie were performed by high temperature treatment of cerium and samarium oxides, preliminary milled through high-energy milling. The synthesis was carried out at 1300 °C.

The phase composition and morphology of the samples were elucidated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Infrared spectroscopy (FTIR) was used to study the structure of the samples. X-ray photoelectron spectroscopy (XPS) was performed to verify the presence of  $Ce^{3+}$  ions in the final powders.

The obtained results demonstrate the possibility for preparation of Sm – doped ceria with different molar ratios by ionic gelation technique at relatively low synthesis temperature (about 500 °C) compared to the conventional high temperature method (about 1300 °C).

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## Low temperature synthesis of PtSe<sub>2</sub> and PtTe<sub>2</sub> nanolayers

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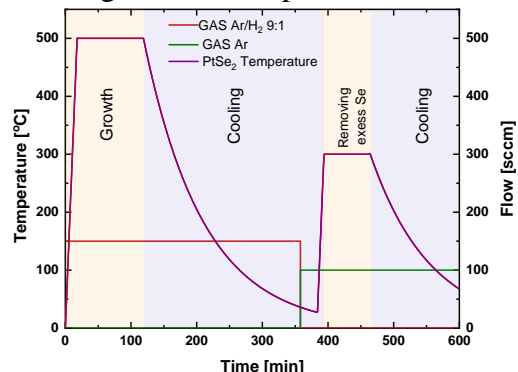
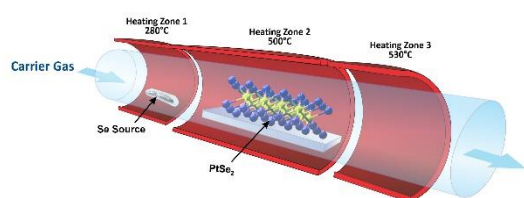
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Transition metal dichalcogenides (TMDC) are new family of atomically thin materials, represented by chemical formula MX<sub>2</sub> (M= transition metal and X= S, Se, Te). Usually, TMDC are layered in nature, having strong covalent bonds between the atoms of a single layer while the interaction of adjacent layers is mediated by weak van der Waals (vdW) forces. As a result, TMDCs possess tunable band gaps in the range 1-2 eV, making them valuable in a wide range of heterostructure based electronic devices and catalysts. Precise tuning of the band gap can be done by controlling the number of layers or by using strain in some cases [2].

Here we report the synthesis details of PtSe<sub>2</sub> and PtTe<sub>2</sub> layers by selenization of pre-deposited Pt films using thermal assisted conversion (TAC) method at atmospheric pressure and on a glass substrate. The results are confirmed by XPS and Raman analysis. The layers were further investigated with AFM and optical transmittance, revealing thickness dependence.



**Figure 1:** Synthesis of 2D PtSe<sub>2</sub> via direct selenization (left) and thermal map of the process (right)

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## Transformation of powder-pasted and electroplated zinc active mass after cycling in Ni-Zn battery cells

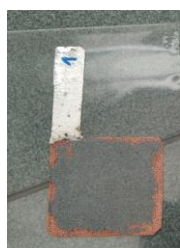
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Research interest in Ni-Zn secondary batteries has increased in recent years due to a number of their advantages over other batteries of a similar type, such as Li-ion. Despite their safer nature, competitive power density and low cost, rechargeable alkaline zinc systems have not penetrated deeply into the market due to a number of difficulties arising from the solubility of the Zn electrode in the alkaline solution. Performance limiting issues mainly include: passivation during the discharge process, shape changes, dendrite formation (during charging), Zn corrosion, etc. The abovementioned characteristics leading to poor cycle life of Ni-Zn batteries provoke a need for a detailed study of the changes occurring of the anode active material, which in turn is closely related to the electrochemical characteristics of the final electrode assembly.

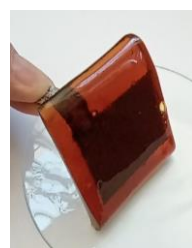
The aim of the present work is to visualize the shape changes, taking place on the surface of the electrodes and to elucidate the morphology and phase composition of zinc active mass in two types of Ni-Zn battery cells before and after cycling. The cathode material in the cells under study is commercially available sintered NiOOH, while the anode material is prepared by two techniques: (i) by Zn powder with AGAR binder, pasted on the copper foam current collector (Fig. 1); (ii) by electroplating of Zn on the copper foam current collector (Fig. 2). As an electrolyte, potassium hydroxide being immobilized in a commercially available separator Celgard<sup>®</sup> 3501 or in a gel, prepared from PVA with appropriate additives, was used.



a.)



b.)



c.)



d.)

**Figure 1:** Zn anode (Zn powder + AGAR binder) initial (a) and after 450 cycles (b).

**Figure 2:** Zn anode (electroplated Zn on Cu foam) initial (a) and after cycling 500 cycles (b).

The obtained results demonstrate that the cycling life of the cells is limited by asymmetrical rearrangement of zinc for the first cell, and by growth of dendrites and degradation of the polymer electrolyte for the second cell. Improvements in the performance and the reproducibility of the cells are under investigation.

**Acknowledgements:** The authors kindly acknowledge the financial support of project № BG05M2OP001-1.002-0014 „Center of competence HITMOBIL - Technologies and systems for generation, storage and consumption of clean energy”, funded by Operational Programme “Science and Education for Smart Growth” 2014-2020, co-funded by the EU from European Regional Development Fund.

## Investigation of the physicochemical and electrochemical behaviour of heat-treated shungite

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The mineral shungite is an intermediate form between amorphous carbon and graphite crystal containing carbon (30%), silica (45%) and silicate mica (about 20%). On the basis of shungite were created new conductive paints, fillers for plastic materials, substitutes for rubber and soot, composite materials, concrete, bricks, putty plasters, asphalts, as well as materials with bactericidal reactivity. The wide range properties of shungite determines the opportunity for new areas of industrial application of this mineral in science and technology, which contributes to more in-depth study of the structure with the help of modern analytical methods.

In the present work, heat-treated shungite samples were used under the same conditions in a high temperature furnace at 400 °C, 800 °C and 1200 °C. The samples were examined in terms of: surface morphology (SEM), structure (XRD), electrochemical properties and determination of a specific surface (BET).

The samples were tested electrochemically in lithium half-cell configuration using 1M LiFP<sub>6</sub> in EC:DMC (1:1) electrolyte, counter electrode of metal lithium foil and Whatman GF/C separator. Among all tested materials, the untreated sample appears to deliver highest initial specific capacity (442 mAh g<sup>-1</sup>) in the galvanostatic test, followed by samples thermally treated at 400 °C (271 mAh g<sup>-1</sup>), 800 °C (260 mAh g<sup>-1</sup>) and 1200 °C (135 mAh g<sup>-1</sup>).

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