

## МОДУЛ 1

### 1. Заглавие Development of New Antimycobacterial Sulfonyl Hydrazones and 4-Methyl-1,2,3-thiadiazole-Based Hydrazone Derivatives

**Автори:** V. Angelova, T. Pencheva, N. Vassilev, E. Yovkova, R. Mihaylova, B. Petrov, V. Valcheva

**Резюме** Fifteen 4-methyl-1,2,3-thiadiazole-based hydrazone derivatives **3a–d** and sulfonyl hydrazones **5a–k** were synthesized. They were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C NMR, and HRMS. *Mycobacterium tuberculosis* strain H37Rv was used to assess their antimycobacterial activity. All compounds demonstrated significant minimum inhibitory concentrations (MIC) from 0.07 to 0.32 μM, comparable to those of isoniazid. The cytotoxicity was evaluated using the standard MTT-dye reduction test against human embryonic kidney cells HEK-293T and mouse fibroblast cell line CCL-1. 4-Hydroxy-3-methoxyphenyl substituted 1,2,3-thiadiazole-based hydrazone derivative **3d** demonstrated the highest antimycobacterial activity (MIC = 0.0730 μM) and minimal associated cytotoxicity against two normal cell lines (selectivity index SI = 3516, HEK-293, and SI = 2979, CCL-1). The next in order were sulfonyl hydrazones **5g** and **5k** with MIC 0.0763 and 0.0716 μM, respectively, which demonstrated comparable minimal cytotoxicity. All compounds were subjected to ADME/Tox computational predictions, which showed that all compounds corresponded to Lipinski's Ro5, and none were at risk of toxicity. The suitable scores of molecular docking performed on two crystallographic structures of enoyl-ACP reductase (InhA) provide promising insight into possible interaction with the InhA receptor. The 4-methyl-1,2,3-thiadiazole-based hydrazone derivatives and sulfonyl hydrazones proved to be new classes of lead compounds having the potential of novel candidate antituberculosis drugs.

**Списание:** [Antibiotics 11\(5\) \(2022\) 562](#)

### 2. Заглавие Obtaining abrasives on the base of composite Ni-P coatings for surface treatment of rock materials

**Автори** V. Chakarova, M. Petrova

**Резюме** The electroless deposition of Ni-P coatings is well known classic method for production of metal coatings on polymers. The addition of dispersed particles of different types and sizes to the base solution for electroless deposition significantly improves the properties of the coating by increasing its wear resistance and micro-hardness. Thereby, the metallized polymers find new and different applications. By using a device, designed and developed in IPC-BAS, tribological tests of composite Ni-P coatings deposited on substrate of polyethylene terephthalate (PET) are performed. Three types of dispersed particles (diamond (D), BN and

SiC) are co-deposited in the Ni-P coatings. Their application as abrasive material for surface treatment of rock materials is evaluated. The structure, morphology and elemental composition of Ni-P coatings are characterized by SEM and EDS.

**Списание** [Proceedings of the XIX International Scientific Congress Machines, Technologies, Materials 1 \(2022\) 81](#)

**3. Заглавие** Nucleic acid-based supramolecular structures: vesicular spherical nucleic acids from a nonphospholipid nucleolipid

**Автори** E. Dimitrov, N. Toncheva-Moncheva, P. Bakardzhiev, A. Forys, J. Doumanov, K. Mladenova, S. Petrova, B. Trzebicka, S. Rangelov

**Резюме** Vesicular spherical nucleic acids are dynamic nucleic acid-based supramolecular structures that are held together via non-covalent bonds. They have promising applications as drug and nucleic acid delivery materials, diagnostic and imaging tools and platforms for development of various therapeutic schemes. In this contribution, we report on vesicular spherical nucleic acids, constructed from a non-phospholipid nucleolipid – an original hybrid biomacromolecule, composed of a hydrophobic residue, resembling that of the naturally occurring phospholipids, and a DNA oligonucleotide strand. The nucleolipid was synthesized by coupling of dibenzocyclooctyne-functionalized oligonucleotide and azidated 1,3-dihexadecyloxy-propane-2-ol via an azide–alkyne click reaction. In aqueous solution it spontaneously self-associated into nanosized supramolecular structures, identified as unilamellar vesicles composed of a self-closed interdigitated bilayer. Vesicular structures were also formed upon intercalation of the nucleolipid via its lipid-mimetic residue in the phospholipid bilayer membrane of liposomes prepared from readily available and FDA-approved lipids (1,2-dipalmitoyl-rac-glycero-3-phosphocholine and cholesterol). The vesicular structures are thoroughly investigated by light scattering (dynamic, static, and electrophoretic) and cryogenic TEM and the physical characteristics, in particular, number of strands per particle, grafting density, and conformation of the strands, were compared to those of reference spherical nucleic acids. Finally, the vesicular structures were shown to exhibit cellular internalization with no need of transfection agents and enhanced colloidal and nuclease stability

**Списание** [Nanoscale Adv. 2022 \(4\) 3793](#)

**4. Заглавие** Structural and optical properties of MgMoO<sub>4</sub> prepared by mechanochemical technique

**Автори** M.Gancheva, T. Rojac, R. Iordanova, I. Piroeva, P. Ivanov

**Резюме** MgMoO<sub>4</sub> with hexagonal particles were prepared by combining high energy ball milling with heat treatment technique. The influence of the mechanochemical activation/heat-treatment on the phase, structural and morphology transformation were investigated by X-ray powder diffraction analysis (XRD), infrared spectroscopy (IR), differential scanning calorimetry (DSC), particle size distribution (PSD) and scanning electron microscope (SEM). Optical properties of the final product were studied by UV–Vis and photoluminescence (PL) measurements. Mechanochemical activation of the initial oxides for 10 h ball milling leads to a full amorphization of MoO<sub>3</sub>, only. The heat-treatment at different temperatures after 10 h milling time results to the phase formation of MgMoO<sub>4</sub>. The reaction started at 400 °C for 5 h and completed at 800 °C for 5 h. The calculated energy band gap value as prepared MgMoO<sub>4</sub> is 2.03 eV and exhibits photoluminescence emission above 600 nm. The CIE chromaticity coordinates (x = 0.53 and y = 0.43) were found to lie in the orange region.

**Списание** [Ceram Int 48\(15\) \(2022\) 17149](#)

**5. Заглавие** Structural characterization of polysaccharides from *Geranium sanguineum* L. and their immunomodulatory effects in response to inflammatory agents

**Автори** Y. Georgiev, B. Dzhambazov, T. Batsalova, O. Vasicek, L. Dobрева, P. Denev, S. Danova, S. Simova, C. Wold, M. Ognyanov, B. Paulsen, A. Krastanov

**Резюме** Ethnopharmacological relevance: *Geranium sanguineum* L. is used for treatment of inflammations, anemia, malignant diseases of the blood-forming organs, diarrhea, respiratory infections, etc. Only flavonoids in root extracts have been elucidated as immunostimulating and anti-inflammatory compounds, and polysaccharides in the herb have not been examined. Aim of the study: to compare the chemical features of polysaccharide complexes (PSCs) from leaves (GSL-PSC) and roots (GSR-PSC) of *G. sanguineum*, as well as their immunomodulatory activities on leukocytes after inflammation, and effects on the growth of different bacteria. Materials and methods: The samples were isolated by water extraction and their structural features were studied by 2D NMR spectroscopy. The stimulatory effects of both PSCs on human leukocytes were analyzed with flow cytometry. Their suppressive activities on the oxidative burst in blood and derived neutrophils against opsonized zymosan and phorbol myristate acetate were investigated. The effects of the samples on viability, NO and interleukin 6 (IL-6) syntheses in RAW264.7 cells after inflammation with lipopolysaccharides (LPS) were tested. The prebiotic and anti-biofilm activities of the PSCs were evaluated. Results: The total carbohydrate content in the samples was significant (73.6–76.8%). GSL-PSC contained pectins, which were rich in homogalacturonan (HG), and smaller amounts of rhamnogalacturonan (RG) type I, decorated by 1,5- $\alpha$ -L-Araf, 1,4- and 1,6- $\beta$ -D-Galp chains. GSR-PSC contained starch, followed by pectins with lower HG content and more RG-I regions, substituted by 1  $\rightarrow$  3,5- $\alpha$ -L-arabinans and 1  $\rightarrow$  3,6- $\beta$ -D-galactans. GSL-PSC and GSR-PSC (200  $\mu$ g/mL) increased monocyte and granulocyte cell counts, but GSR-PSC also elevated T helper and B cell levels in a normal and activated state. GSR-PSC triggered a dose-dependent (50–200  $\mu$ g/mL) oxidative burst in blood, but alleviated it after inflammation even in blood-derived neutrophils.

It was free of LPS, and activated NO and IL-6 productions in RAW264.7 cells better than GSL-PSC, without affecting their viability. Both PSCs (2.0%, w/v) stimulated probiotic co-cultures between *Clostridium beijerinckii* strains and *Lactobacillus* sp. ZK9, and inhibited the growth and biofilm formation of *Escherichia coli*, *Streptococcus mutans* and *Salmonella enterica*. Conclusions: The PSs in *G. sanguineum* could be involved in the stimulatory effects on blood-forming organs and anti-inflammatory action of aqueous root extracts in case of infections. These PSs should be included in synbiotic foods to support the treatment of inflammations and infections in the gut.

Списание [J. Ethnopharmacology 294\(10\) \(2022\)115390](#)

## 6. **Заглавие** Structural Features and Immunomodulatory Effects of Water-Extractable Polysaccharides from *Macrolepiota procera* (Scop.) Singer

**Автори** Y. Georgiev, O. Vasicek, B. Dzhabazov, T. Batsalova, P. Denev, L. Dobрева, S. Danova, S. Simova, C. Wold, M. Ognyanov, B. Paulsen, A. Krastanov

**Резюме** *Macrolepiota procera* (MP) is an edible mushroom used in the treatment of diabetes, hypertension and inflammation. However, the structure and biological effects of its polysaccharides (PSs) are unclear. This study investigates the structural features of a PS complex from MP (MP-PSC), its immunomodulatory activities and effects on probiotic and pathogenic bacteria. MP-PSC was obtained by boiling water, and PSs were characterized by 2D NMR spectroscopy. The immunomodulatory effects on blood and derived neutrophils, other leukocytes, and murine macrophages were studied by flow cytometry, chemiluminescence, spectrophotometry, and ELISA. The total carbohydrate content of MP-PSC was 74.2%, with glycogen occupying 36.7%, followed by  $\beta$ -D-glucan,  $\alpha$ -L-fuco-2-(1,6)-Dgalactan, and  $\beta$ -D-glucomannan. MP-PSC (200  $\mu$ g/mL) increased the number of CD14<sup>+</sup> monocyte cells in the blood, after ex vivo incubation for 24 h. It dose-dependently (50–200  $\mu$ g/mL) activated the spontaneous oxidative burst of whole blood phagocytes, NO, and interleukin 6 productions in RAW264.7 cells. MP-PSC exhibited a low antioxidant activity and failed to suppress the oxidative burst and NO generation, induced by inflammatory agents. It (2.0%, w/v) stimulated probiotic co-cultures and hindered the growth and biofilm development of *Escherichia coli*, *Streptococcus mutans* and *Salmonella enterica*. MP PSs can be included in synbiotics to test their immunostimulating effects on compromised immune systems and gut health.

Списание [Fungi 8 \(2022\) 848](#)

## 7. **Заглавие** Hollow Spherical Nucleic Acid Structures Based on Polymer Coated Phospholipid Vesicles

**Автори** E. Haladjova, M. Petrova, I. Ugrinova, A. Forysc, B. Trzebicka, S. Rangelov

**Резюме** A feasible one pot synthesis of hollow spherical nucleic acids (SNAs) using phospholipid liposomes is reported. These constructs are synthesized in a chemically straightforward process involving formation of unilamellar liposomes, coating the liposomes with a thin cross-linked polymeric layer, and grafting the latter with short (about 20 bases) DNA oligonucleotide strands. They consist of vesicular cores, composed of readily available phospholipid (1,2-dipalmitoyl-sn-glycerophosphocholine), whereas the strands are deliberately arranged on the surface of the vesicular entities. The initial vesicular structure and morphology are preserved during the coating and grafting reactions. The novel hollow/vesicular SNAs are characterized with a hydrodynamic radius and radius of gyration of 78.3 and 88.5 nm, respectively, and moderately negative ( $-14.2$  mV)  $\zeta$  potential. They carry thousands (5868) of oligonucleotide strands per vesicle, which are not strongly radially oriented and adopt an unextended conformation as anticipated from the smaller value of the grafting density compared to the critical grafting density at the transition to brush conformation. The constructs are practically devoid of toxicity and exhibit high binding affinity to complementary nucleic acids. Unlike any other nucleic acid structural motif, they cross the cell membrane and enter cells without the need of transfection agents.

**Списание** [Soft Matter 18\(29\) \(2022\) 5426](#)

## **8. Заглавие** Functional Polyion Complex Micelles for Potential Targeted Hydrophobic Drug Delivery

**Автори** R. Kalinova, I. Dimitrov

**Резюме** Polyion complex (PIC) micelles have gained an increasing interest, mainly as promising nano-vehicles for the delivery of various hydrophilic charged (macro)molecules such as DNA or drugs to the body. The aim of the present study is to construct novel functional PIC micelles bearing cell targeting ligands on the surface and to evaluate the possibility of a hydrophobic drug encapsulation. Initially, a pair of functional oppositely charged peptide-based hybrid diblock copolymers were synthesized and characterized. The copolymers spontaneously co-assembled in water into nanosized PIC micelles comprising a core of a polyelectrolyte complex between poly(L-aspartic acid) and poly(L-lysine) and a biocompatible mixed shell of disaccharide-modified poly(ethylene glycol) and poly(2-hydroxyethyl methacrylate). Depending on the molar ratio between the oppositely charged groups, PIC micelles varying in surface charge were obtained and loaded with the natural hydrophobic drug curcumin. PIC micelles' drug loading efficiency, in vitro drug release profiles and antioxidant activity were evaluated. The preliminary results indicate that PIC micelles can be successfully used as carriers of hydrophobic drugs, thus expanding their potential application in nanomedicine.

**Списание** [Molecules 27\(7\) \(2022\) 2178](#)

## 9. **Заглавие** Redox-Responsive Crosslinked Mixed Micelles for Controllable Release of Caffeic Acid Phenethyl Ester

**Автори** К. Kamenova, G. Grancharov, V. Kortenova, P. Petrov

**Резюме** We report the elaboration of redox-responsive functional micellar nanocarriers designed for triggered release of caffeic acid phenethyl ester (CAPE) in cancer therapy. Three-layered micelles, comprising a poly( $\epsilon$ -caprolactone) (PCL) core, a middle poly(acrylic acid)/poly(ethylene oxide) (PAA/PEO) layer and a PEO outer corona, were prepared by co-assembly of PEO113-b-PCL35-b-PEO113 and PAA13-b-PCL35-b-PAA13 amphiphilic triblock copolymers in aqueous media. The preformed micelles were loaded with CAPE via hydrophobic interactions between the drug molecules and PCL core, and subsequently crosslinked by reaction of carboxyl groups from PAA and a disulfide crosslinking agent. The reaction of crosslinking took place in the middle layer of the nanocarriers without changing the encapsulation efficiency (EE~90%) of the system. The crosslinked polymeric micelles (CPMs) exhibited superior structural stability and did not release CAPE in phosphate buffer (pH 7.4). However, in weak acidic media and in the presence of 10 mM reducing agent (dithiothreitol, DTT), the payload was released at a high rate from CPMs due to the breakup of disulfide linkages. The physicochemical properties of the nanocarriers were investigated by dynamic and electrophoretic light scattering (DLS and ELS) and atomic force microscopy (AFM). The rapid release of CAPE under intracellular-like conditions and the lack of premature drug release in media resembling the blood stream (neutral pH) make the developed CPMs a promising candidate for controllable drug release in the microenvironment of tumors.

**Списание** [Pharmaceutics 14\(3\) \(2022\) 679](#)

## 10. **Заглавие** Functional Nanogel from Natural Substances for Delivery of Doxorubicin

**Автори** К. Kamenova, L. Radeva, K. Yoncheva, F. Ublekov, M. Ravutsov, M. Marinova, S. Simeonov, A. Forys, B. Trzebicka, P. Petrov

**Резюме** Nanogels (NGs) have attracted great attention because of their outstanding biocompatibility, biodegradability, very low toxicity, flexibility, and softness. NGs are characterized with a low and nonspecific interaction with blood proteins, meaning that they do not induce any immunological responses in the body. Due to these properties, NGs are considered promising candidates for pharmaceutical and biomedical application. In this work, we introduce the development of novel functional nanogel obtained from two naturally based products—citric acid (CA) and pentane-1,2,5-triol (PT). The nanogel was synthesized by precipitation esterification reaction of CA and PT in tetrahydrofuran using N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide (EDC) and 4-(dimethylamino)pyridine (DMAP) catalyst system. Dynamic light scattering (DLS), cryogenic transmission electron microscopy (cryo-TEM) and atomic force microscopy (AFM) analyses revealed formation of spherical nanogel particles with a negative surface charge. Next, the nanogel was loaded with doxorubicin

hydrochloride (DOX) by electrostatic interactions between carboxylic groups present in the nanogel and amino groups of DOX. The drug-loaded nanogel exhibited high encapsulation efficiency (EE~95%), and a bi-phasic release behavior. Embedding DOX into nanogel also stabilized the drug against photodegradation. The degradability of nanogel under acidic and neutral conditions with time was investigated as well.

Списание [Pharmaceutics 14 \(2022\) 679](#)

**11. Заглавие** Biological Activity and NMR-Fingerprinting of Balkan Endemic Species *Stachys thracica* Davidov

**Автори** D. Mantovska, M. Zhiponova, M. Georgiev, K. Alipieva, I. Tsacheva, S. Simova, P. Yordanova

**Резюме** *Stachys thracica* Davidov is a Balkan endemic species distributed in Bulgaria, Greece, and Turkey. In Bulgaria, it is classified as “rare” and is under the protection of the Bulgarian biodiversity law. The aim of our study was to develop an efficient protocol for ex situ conservation of *S. thracica* and to perform comparative NMR-based metabolite profiling and bioactivity assays of extracts from in situ grown, in vitro cultivated, and ex vitro acclimated plants. Micropropagation of *S. thracica* was achieved by in vitro cultivation of mono-nodal segments on basal MS medium. Ex vitro adaptation was accomplished in the experimental field with 83% survival while conserved genetic identity between in vitro and ex vitro plants as shown by the overall sequence-related amplified polymorphism marker patterns was established. Verbascoside, chlorogenic acid, and trigonelline appeared the main secondary metabolites in in situ, in vitro cultivated, and ex vitro acclimated *S. thracica*. High total phenolic and flavonoid content as well as antioxidant and radical scavenging activity were observed in in situ and ex vitro plants. Further, the anti-inflammatory activity of *S. thracica* was tested by hemolytic assay and a high inhibition of the complement system was observed. Initiated in vitro and ex vitro cultures offer an effective tool for the management and better exploitation of the *Stachys* secondary metabolism and the selection of lines with high content of bioactive molecules and nutraceuticals.

Списание [Metabolites 12\(3\) \(2022\) 251](#)

**12. Заглавие** Dinuclear vs. Mononuclear Copper(II) Coordination Species of Tylosin and Tilmicosin in Non-Aqueous Solutions

**Автори** I. Pantcheva, R. Stamboliyska, N. Petkov, A. Tadjer, S. Simova, R. Stoyanova, R. Kukeva, P. Dorkov

**Резюме** The veterinary 16-membered macrolide antibiotics tylosin (HTyl, 1a) and tilmicosin (HTilm, 1b) react with copper(II) ions in acetone at metal-to-ligand molar ratio of 1:2 to form blue (2) or green (3) metal(II) coordination species, containing nitrate or chloride anions, respectively. The complexation processes and the properties of 2–3 were studied by an assortment of physicochemical techniques (UV-Vis, EPR, NMR, FTIR, elemental analysis). The experimental data revealed that the main portion of copper(II) ions are bound as neutral EPR-silent dinuclear complexes of composition  $[\text{Cu}_2(\mu\text{-NO}_3)_2\text{L}_2]$  (2a–b) and  $[\text{Cu}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{HL})_2]$  (3a–b), containing impurities of EPR-active mono-species  $[\text{Cu}(\text{NO}_3)\text{L}]$  (2a'–b') and  $[\text{CuCl}_2(\text{HL})]$  (3a'–b'). The possible structural variants of the dinuclear- and mono-complexes were modeled by the DFT method, and the computed spectroscopic parameters of the optimized constructs were compared to those measured experimentally. Using such a combined approach, the main coordination unit of the macrolides, involved in the complex formation, was defined to be their mycaminosyl substituent, which acts as a terminal ligand in a bidentate mode through the tertiary nitrogen atom and the oxygen from a deprotonated (2) or non-dissociated (3) hydroxyl group, respectively.

Списание [Molecules 27\(12\) \(2022\) 3899](#)

**13. Заглавие** Effect of the reaction medium modification on the chemical and phase composition and morphological characteristics of biomimetically synthesized calcium phosphate ceramic powders

**Автори** K. Sezanova, P. Shestakova, R. Gergulova, D. Rabadjieva, Y. Mitrev, S. Teravitcharova

**Резюме** The effect of two modifiers (glycerin and xanthan gum) of the reaction medium consisting of simulated body fluid and glycine buffer, on the composition and morphology of the obtained precursors and particle size distribution of their high-temperature phases was followed. The modifiers were used in order to prevent the growth of primary nuclei. The results showed that glycerin and xanthan gum did not affect the chemical and phase composition of either the precursors or the high-temperature phases. They influenced the shape of the primary precipitated particles and the specific surface area of the precursors, as well the particle size distribution of the calcined products. Copyright 2022 Elsevier Ltd. All rights reserved. Selection and peer-review under responsibility of the scientific committee of the Third Workshop on Size-Dependent Effect in Materials for Environmental Protection and Energy Application.

Списание [Mater Today: Proc 61 \(2022\) 1226](#)

**14. Заглавие** Research on properties and catalytic behaviour in CO hydrogenation at atmospheric and high pressure of bimetallic systems (10%Co+0.5%Pd)/TiO<sub>2</sub> (Al<sub>2</sub>O<sub>3</sub>)

**Автори** М. Shopska, А. Caballero, F. Platero, S. Todorova, К. Tenchev, М. Fabian, К. Aleksieva, Н. Kolev, G. Kadinov

**Резюме** The properties of prereduced (10%Co+0.5%Pd)/Al<sub>2</sub>O<sub>3</sub> (TiO<sub>2</sub>) systems in the CO hydrogenation reaction at atmospheric and high pressure were studied. At atmospheric pressure, alumina-supported catalysts were more selective toward methane but those using titania were more active. Alumina containing samples demonstrated high temperature H<sub>2</sub> desorption, firmly held surface carbonate species, high tendency to agglomeration. During the reaction metal surface reconstruction and increased formation of CH<sub>2</sub> groups occurred being more pronounced with titaniasupported catalysts. Stability tests at 250 °C showed opposite behaviour of both systems. Monodentate carbonate intermediates adsorbed on sites of moderate strength prevailed on titania samples, while formate species predominated on high strength sites of alumina-supported catalysts. High pressure catalytic tests revealed dependence of activity on Tred, synthesis of C<sub>2</sub>+ hydrocarbons, decreased CO<sub>2</sub> production, a higher CH<sub>4</sub>/CO<sub>2</sub> ratio for alumina containing system. Due to SMSI, increased CO<sub>2</sub> production on titania samples was preserved. Titania-supported catalysts revealed a stronger decrease of CO conversion rising Tred while alumina catalysts had almost unchanged activity. CO conversion decreased with time due to difficulties in surface diffusion of reagents/intermediates/products and metal particle agglomeration. Concerning Tred comparison of product distribution showed a steady trend. Because of stable CO and CH<sub>x</sub> surface species, titania containing catalysts produced lower content of C<sub>5</sub>+ compounds. Alumina-supported samples showed a higher selectivity to C<sub>5</sub>+ compounds at the expense of methane. A higher selectivity ratio for CH<sub>4</sub> and CO<sub>2</sub> determined in catalytic CO hydrogenation over a certain catalyst at atmospheric pressure could indicate that a given sample is predisposed to form C<sub>2</sub>+ hydrocarbons at a higher pressure.

**Списание** [React Kinet Mech Catal 135 \(2022\) 589](#)

**15. Заглавие** The effect of experimental conditions in root dentin microcracks detection by micro-computed tomography

**Автори** D. Tatchev, I. Tsenova-Ilieva, T. Vassilev, E. Karova

**Резюме** The aim of the study was to assess the effect of different experimental conditions on registration of microcracks by means of micro-computed tomography. Twenty roots of permanent lower incisors were instrumented with SAF system, filled with a single-cone technique and retreated with the Pro Taper Universal Retreatment system. Each sample was measured in dry, water, and moist conditions. The dry scanning was done after drying of the roots for a period of 4 h in ambient conditions followed by a second observation in wet environment after 48 h of rehydrating in distilled water. A time scan was performed to measure the dentin shrinkage while drying the samples in the tomograph's device compartment. All roots underwent complex inhomogeneous shrinkage and deformation due to the internal stress upon dehydration. This deformation opened the existing cracks to an extent above the current

resolution of today's laboratory computed tomography scanners. Contrary, rehydration of the dentin reversed the deformation thus closing some of the cracks below the computed tomography resolution making them undetectable. The first dehydration of dentin may be a source of cracks initiation itself.

Списание [J Mech Behavior Biomed Materials 128 \(2022\) 105108](#)

#### 16. **Заглавие** CO<sub>2</sub> Adsorption on the N- and P-Modified Mesoporous Silicas

**Автори** О. Tumurbaatar, H. Lazarova, M. Popova, V. Mitova, P. Shestakova, N. Koseva

**Резюме** SBA-15 and MCM-48 mesoporous silicas were modified with functionalized (3-aminopropyl) triethoxysilane (APTES) by using the post-synthesis method, thus introducing N- and P-containing groups to the pore surface. The structure of the newly synthesized modifiers (aldimine and aminophosphonate derivatives of (3-aminopropyl)triethoxysilane and their grafting onto the porous matrix were proved by applying multinuclear NMR and FTIR spectroscopies. The content of the grafted functional groups was determined via thermogravimetric analysis. The physicochemical properties of the adsorbent samples were studied by nitrogen physisorption and UV–Vis spectroscopy. The adsorption capacity of CO<sub>2</sub> was measured in a dynamic CO<sub>2</sub> adsorption regime. The modified silicas displayed an enhanced adsorption capacity compared to the initial material. The <sup>13</sup>C NMR spectra with high-power proton decoupling proved the presence of physically captured CO<sub>2</sub>. A value of 4.60 mmol/g was achieved for the MCM-48 material grafted with the Schiff base residues. The total CO<sub>2</sub> desorption was achieved at 40 °C. A slight decrease of about 5% in CO<sub>2</sub> adsorption capacities was registered for the modified silicas in three adsorption/desorption cycles, indicating their performance stability

Списание [Nanomaterials 12 \(2022\) 1224](#)

#### 17. **Заглавие** Porous metallic structures by de-alloying microcrystalline melt-spun ternary Zn<sub>70</sub>(Sn,Bi)<sub>30</sub>

**Автори** E. Vassileva, L. Mihaylov, M. Spassova, T. Spassov

**Резюме** A rapid solidification method (melt-spinning technique) was applied to produce a series of Zn<sub>70</sub>Sn<sub>30-x</sub>Bi<sub>x</sub> (x = 5,15,30) ribbons with homogeneous microcrystalline structure. All alloys contained ternary eutectics in a different amount depending on their overall composition, as Zn<sub>70</sub>Sn<sub>15</sub>Bi<sub>15</sub> was characterized with maximum quantity of the ternary eutectic colonies. The as-quenched alloys in the form of ribbons were subjected to selective electrochemical dissolution (de-alloying), which resulted in mechanically stable three-dimensional porous structures. It was found that both, the morphology and size of the pores and ligaments depend on the initial alloys' composition and microstructure. The fine initial alloys microstructure (grain size < 200nm) produced by rapid solidification resulted in pores and ligaments in the

nanometric range. The Bi-richest porous alloy revealed a morphology similar to that of human bones, while the porous alloys produced from  $Zn_{70}Sn_{25}Bi_5$  and  $Zn_{70}Sn_{15}Bi_{15}$  were characterized by a worm-like ligament structure. The results obtained pave the way for the formation of useful for practical applications porous structures (e.g., for ion batteries electrodes) by de-alloying microcrystalline eutectic alloys with a suitable phase composition.

Списание [J Porous Materials 10934 \(2022\) 1361](#)

### **18. Заглавие** Evolution of WSe<sub>2</sub> Flakes Synthesized by Thermally Assisted Conversion Method

**Автори** V. Marinova, K. Buchkov, V. Videva, I. Dionisiev, N. Minev, V. Strijkova, D. Dimov, H. Dikov, I. Avramova, P. Rafailov, D. Dimitrov

**Резюме** We report the synthesis of tungsten diselenide (WSe<sub>2</sub>) flakes and continuous layers using an atmospheric pressure thermally assisted conversion (TAC) method, where the tungsten (W) layers were pre-deposited by a magnetron sputtering system onto fused silica substrates. Optical microscopy (OM) and 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 fused silica substrates. Raman spectroscopy and photoluminescence measurements confirmed the existence of atomically thin flakes and 2H-WSe<sub>2</sub> continuous layers. The measured current–voltage characteristics indicated Ohmic behavior under dark conditions and photo illumination. Finally, the demonstrated resistor-like behavior suggested unlimited prospects for WSe<sub>2</sub> integration into a variety of heterostructures.

Списание [Coatings 12 \(2022\) 353](#)

### **19. Заглавие** Optical Properties of WSe<sub>2</sub> Thin Flakes

**Автори** I. Dionisiev, N. Minev, V. Videva, V. Strijkova, H. Dikov, P. Rafailov, D. Dimitrova, V. Marinova

**Резюме** The paper reports synthesis details of 2D WSe<sub>2</sub> flakes, grown at short pre-deposition time of W layer/clusters subsequently followed by selenization using Thermally Assisted Conversion (TAC) method. Atomic Force Microscopy (AFM) and Raman analysis reveal the formation of different flake shapes (mainly dendritic and triangular) with typical Raman modes for ultrathin films close to the monolayer limit.

Списание [XXXI International Scientific Conference Electronics \(ET\) \(2022\) 1](#)

### **20. Заглавие** 2D PtTe<sub>2</sub> Layers Synthesized by Thermally Assisted Conversion Method

**Автори** N. Minev, I. Dionisiev, K. Buchkov, H. Dikov, V. Videva, V. Strijkova, P. Rafailov, D. Dimitrov, V. Marinova

**Резюме** Scalable production and controlled doping of large-area two-dimensional transition-metal dichalcogenide films are fundamental steps toward their applications in electronic and opto-electronic devices. Although a variety of methods for preparation of wafer-scale transition-metal dichalcogenide films have been developed, they still need further elaboration to satisfy the high quality requirements for application-grade materials. Here we report the synthesis of 2D PtTe<sub>2</sub> by direct tellurization of pre-deposited thin Pt film of various thickness on soda lime glass substrates.

**Списание** [XXXI International Scientific Conference Electronics \(ET\) \(2022\) 1](#)

## **21. Заглавие** Organic random laser generation by stimulated cascaded four-wave mixing

**Автори** H. Kisov, K. Blagoev, V. Tankova, B. Georgieva, V. Strijkova, P. Petrova, G. Dyankov

**Резюме** Our study investigated the nonlinear lasing properties of a solid-state dye laser. Laser emission was provided by light amplification in static disordered nanostructures with the gain based on a xanthene dye-functionalized epoxy resin polymer. The emission spectrum was found to be reproducible at each near-threshold excitation pulse. We consider that this spectrum results from a non-degenerate cascaded four-wave mixing in the investigated gain medium. The pump beams were generated simultaneously in the bulk isotropic active medium by single-shot excitation on the nanosecond time scale. The downshift and upshift modes were generated via their coherent pump beams. To our knowledge, this type of stimulated highly nondegenerate cascaded four-wave mixing in the visible spectral range (486 nm – 680 nm) has not been experimentally demonstrated before in a random gain medium.

**Списание** [Opt Laser Technol 148 \(2022\) 107766](#)

## **22. Заглавие** In-line Geometric Phase Lens Inscribed in Azopolymer Material Using Polarization Holography

**Автори** L. Nedelchev, L. Nikolova, G. Mateev, B. Ivanov, V. Strijkova, D. Nazarova, E. Stoykova, K. Choi, J. Park

**Резюме** A polarization-sensitive diffractive optical element was recorded in an azopolymer thin film using polarization holography. It acts as a converging lens for left circularly polarized light and as diverging lens for right circularly polarized light.

**Списание** [Technical Digest Series, Optica Publishing Group \(2022\) Th2A.13](#)

**23. Заглавие** Optical response evaluation of azopolymer thin solid films doped with gold nanoparticles with different sizes

**Автори** N. Berberova-Buhova, L. Nedelchev, E. Stoykova, D. Nazarova

**Резюме** Azobenzene and azobenzene-containing polymers are intensively studied in the last decades because of their high potential for various applications: polarization holography, holographic optical polarization-sensitive elements, high-density storage by multiplexing, ptychography, etc. In this article are reported studies based on the optical response of azopolymer poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt], (PAZO) thin films with embedded Au spherical nanoparticles with different sizes. We found that effective medium approximations (Maxwell-Garnett and Bruggeman) are not satisfactory in evaluation of films optical response. The complex refractive index of the composite film is evaluated as a dependence on three factors: 1) the PAZO matrix complex refractive index; 2) volume scattering efficiency of the Au particle and 3) the filling factor of the composite film. The scattering of a single particle in the azopolymer matrix is calculated using the exact vector Maxwell equations. The particles with mean radius 10, 30 and 50 nm are treated as ensemble of non-aggregated spheres. Multiple scattering by individual particles was ignored. Three specific filling factors of 0.008, 0.010 and 0.030 are considered. The optical transmittance and absorption of a 440 nm thick composite film were evaluated. The algorithm is efficient and the results are robust. The photoinduced spectral response of the composite layers is under study.

**Списание** [J Chem Technol Metallurgy 57 \(4\) \(2022\) 671](#)

**24. Заглавие** Europium doped glasses from the oxide system CaO-GeO<sub>2</sub>-Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> for LED application

**Автори** I. Koseva, V. Nikolov, M. Gancheva, L. Aleksandrov, P. Ivanov, P. Petrova, R. Jordanova, R.

**Резюме** Europium doped glasses with three different compositions and different dopant concentrations were prepared from the CaO-GeO<sub>2</sub>-Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> system. The influences of Eu<sup>3+</sup> ions concentration on the thermal stability of the glasses were investigated by DTA analyses. The IR spectra display variations in the glass structures depending on the glass composition and dopant concentration. The excitation and emission spectra of all glasses consist of characteristic peaks of Eu<sup>3+</sup> ions. Some changes are observed with the variation of the glass composition and active ion concentration. Chromaticity coordinates of the examined glasses are placed in a relatively narrow area in the red part of the diagram. The obtained results show that europium doped glasses from the oxide system CaO-GeO<sub>2</sub>-Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> can be used for red phosphors. Copyright 2022 Elsevier Ltd. All rights reserved. Selection and peer-review under

responsibility of the scientific committee of the Third Workshop on Size-Dependent Effect in Materials for Environmental Protection and Energy Application.

Списание [Mater Today: Proc 61\(4\) \(2022\) 1198](#)

**25. Заглавие** On the structures and luminescence properties of Eu<sup>3+</sup>-doped Li<sub>2</sub>CaGeO<sub>4</sub>, Ca<sub>2</sub>GeO<sub>4</sub>, and Ca<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub> compounds

**Автори** I. Koseva, V. Nikolov, R. Nikolova, P. Tzvetkov, P. Ivanov, P. Petrova, R. Tomova, N. Kuvandjiev, M. Tarassov

**Резюме** Powder samples of Li<sub>2</sub>CaGeO<sub>4</sub>, Ca<sub>2</sub>GeO<sub>4</sub>, and Ca<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub> doped by 0.5, 1, 2, 3, 4 and 5 at% Eu<sup>3+</sup> relative to the Ca<sup>2+</sup>, were prepared using a conventional solid-state synthesis technique. X-ray diffraction (XRD) analyses confirmed obtaining the pure phases at all dopant concentrations. In parallel, single crystals of the three compounds with the experimentally found optimal Eu<sup>3+</sup> concentration were grown using a flux method. Structural investigation on the single crystals were done with a special attention to the form of the Ca–O polyhedron, the mean Ca–O distance, the Ca–Ca distance in the structure, the distortion degree of the polyhedron, as well as the Eu–Ca substitution site. The main spectral characteristics were analyzed and several relationships between the structural and spectra features were found. The optimal dopant concentration was 3 at% for Ca<sub>2</sub>GeO<sub>4</sub> and 4at% for Ca<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub> and Li<sub>2</sub>CaGeO<sub>4</sub>. Commission Internationale de l'éclairage coordinates of the samples showed emission colours in the red region close to the standard red coordinates and slightly influenced by the active ion concentration. The obtained results showed that europium-doped Li<sub>2</sub>CaGeO<sub>4</sub>, Ca<sub>2</sub>GeO<sub>4</sub>, and Ca<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub> could be used as red phosphors.

Списание [Luminescence 37 \(2022\) 1](#)

**26. Заглавие** Core/Double-Sheath Composite Fibers from Poly(ethylene oxide), Poly(L-lactide) and Beeswax by Single-Spinneret Electrospinning

**Автори** S. Kyuchyuk, D. Paneva, N. Manolova, I. Rashkov, D. Karashanova, N. Markova

**Резюме** The conventional approach for preparation of core-sheath fibers is coaxial electrospinning. Single-spinneret electrospinning of emulsions is a much less common method to obtain core-sheath fibers. Core-sheath structure may be generated by electrospinning of homogeneous blend solutions; however, reports on such cases are still scarce. Herein, the preparation of nanofibrous composites from poly(ethylene oxide) (PEO), poly(L-lactide) (PLA) and beeswax (BW) by single-spinneret electrospinning of their homogeneous blend solutions in chloroform is reported. The produced fibers had core/double-sheath structure with a PEO core, PLA inner sheath and BW outer sheath. This original fiber structure was evidenced by transmission electron microscopy, selective extraction of BW or PEO, and X-ray photoelectron

spectroscopy. The PLA/BW double sheath led to hydrophobicity of the PEO/PLA/BW mats. The tensile tests revealed that PEO/PLA/BW mats had substantially improved mechanical behavior as compared to PEO, PLA and PEO/BW mats. PEO/PLA/BW mats can be used as drug carriers as evidenced by the one-pot incorporation of the model drug 5-nitro-8-hydroxyquinoline (NQ) into the fibrous materials. Microbiological tests showed that PEO/PLA/BW/NQ had antimicrobial activity. Therefore, the new materials are promising for wound healing applications.

Списание [Polymers 14 \(2022\) 5036 \(1\)](#)

**27. Заглавие** Structure and phase composition study of thin TiO<sub>2</sub>:C films deposited by r.f. magnetron sputtering

**Автори** Т. Milenov, D. Karaivanova, O. Angelov, P. Terziyska, G. Avdeev, D. Karashanova, B. Georgieva, K. Genkov, D. Dimov, K. Ivanov, S. Kolev, E. Valcheva

**Резюме** Thin films of TiO<sub>2</sub> doped with carbon were deposited on 15×25×1 mm<sup>3</sup> glass substrates by r.f. magnetron co-sputtering of TiO<sub>2</sub> target and carbon plates on their erosion zone in Ar + air atmosphere (0.5 Pa and 0.6 Pa, respectively). Two different process parameters were varied in different experiments: the total area of the carbon plates (84 mm<sup>2</sup>, 560 mm<sup>2</sup>, 830 mm<sup>2</sup> or 1480 mm<sup>2</sup>) and the radial distance from the center of the circle of the erosion zone with maximum rate of sputtering (2 cm or 4 cm). The as-deposited and annealed (air, 400 °C, 1 h) thin films with thicknesses of 40 – 60 nm were studied by ellipsometry, grazing incidence X-ray diffractometry (GIXRD), Raman spectroscopy, transmission (TEM) and scanning electron microscopies (SEM). The ellipsometric studies revealed the band gap, as well as the tail states and optical constants of the thin films obtained. The GIXRD patterns revealed a mix of amorphous and nanocrystalline anatase and rutile TiO<sub>2</sub> phases in all thin films. The Raman study confirmed this conclusion, but the TEM study showed the presence of some nanocrystalline C<sub>200</sub>O<sub>14</sub>Ti<sub>3</sub>, together with the other TiO<sub>2</sub> phases – brookite and nonstoichiometric TiO<sub>x</sub> phases (anatase and rutile). The effects of annealing at 400 °C in air for 60 min are also discussed.

Списание [J Physics: Conf Series 2240 \(2022\) 1](#)

**28. Заглавие** Structure and Phase Composition Study of Heavy Doped with Carbon Thin Films of TiO<sub>2</sub>:C Deposited by RF Magnetron Sputtering

**Автори** Т. Milenov, P. Terziyska, G. Avdeev, D. Karashanova, B. Georgieva, I. Avramova, K. Genkov, E. Valcheva

**Резюме** The aim of the present research is to study some aspects of the carbon doping of TiO<sub>2</sub> thin films and the influence of low temperature thermal annealing on the phase precipitation in thin films. Thin films of heavily doped with carbon TiO<sub>2</sub> (up to 3 at % C) were deposited on (15 × 25 × 1 mm) glass substrates by r.f. magnetron co-sputtering of TiO<sub>2</sub> target and carbon plates on its erosion zone in Ar + air (residual pressure of 0.5 and 0.6 Pa, respectively) atmosphere. Two different process's parameters were varied in different experiments in order to change the carbon content: the total area of the carbon plates which was 30, 84, 132, 400 and 830 mm<sup>2</sup> ) and the radial distance between the center of the circle of the erosion zone with maximum rate of sputtering which was 2 and 4 cm. The as-deposited and annealed (air, 400°C, 1h) thin films with thickness of 110–150 nm were studied by ellipsometry, grazing incidence X-ray diffractometry (GIXRD), X-ray photoelectron spectroscopy, Raman spectroscopy, transmission and scanning electron microscopies. The GIXRD patterns reveal a mix of amorphous and nanocrystalline anatase and rutile TiO<sub>2</sub> phases for all thin films. The Raman study confirms this conclusion but the TEM and GIXRD studies show presence of nonstoichiometric nanocrystalline phase based on Ti<sub>3</sub>C<sub>2</sub>O<sub>14</sub> together with the other phases of TiO<sub>2</sub>-anatase, rutile and brookite. Similar characterizations were carried out after annealing at 400°C in air for 60 min and the most prominent effects of thermal treatment are discussed.

**Списание** [Russian J Inorg Chem 67 \(2022\) 1509](#)

**29. Заглавие** Benchmarking of Density Functionals for the Description of Optical Properties of Newly Synthesized  $\pi$ -Conjugated TADF Blue Emitters

**Автори** G. Ivanova, N. Bozova, N. Petkov, Cunbin An, Benlin Hu, M. Mutovska, K. Konstantinov, Y. Zagranyski, V. Videva, A. Yordanova, M. Baumgarten, A. Ivanova

**Резюме** Computational modeling of the optical characteristics of organic molecules with potential for thermally activated delayed fluorescence (TADF) may assist markedly the development of more efficient emitting materials for organic light-emitting diodes. Recent theoretical studies in this area employ mostly methods from density functional theory (DFT). In order to obtain accurate predictions within this approach, the choice of a proper functional is crucial. In the current study, we focus on testing the performance of a set of DFT functionals for estimation of the excitation and emission energy and the excited singlet-triplet energy gap of three newly synthesized compounds with capacity for TADF. The emitters are designed specifically to enable charge transfer by  $\pi$ -electron conjugation, at the same time possessing high-energy excited triplet states. The functionals chosen for testing are from various groups ranging from gradientcorrected through global hybrids to range-separated ones. The results show that the monitored optical properties are especially sensitive to how the long-range part of the exchange energy is treated within the functional. The accurate functional should also be able to provide well balanced distribution of the  $\pi$ -electrons among the molecular fragments. Global hybrids with moderate (less than 0.4) share of exact exchange (B3LYP, PBE0) and the meta-GGA HSE06 are outlined as the best performing methods for the systems under study.

They can predict all important optical parameters correctly, both qualitatively and quantitatively.

Списание [Chem Eur J \(2022\) e2021044 \(1\)](#)

**30. Заглавие** Optical properties of nanostructured bimetallic films from the Ag-In and Ag-Sb systems and their surface-enhanced fluorescence application

**Автори** V. Katrova, T. Hristova-Vasileva, A. Atanasova, V. Strijkova, R. Todorov

**Резюме** The possibility for tuned excitation of surface plasmon resonance in Ag-In and AgSb films with different compositions and thicknesses was studied in terms of preparation and microstructural and optical properties. The analyses show that plasmon excitation can be achieved both by changing the thickness of the deposited bimetallic films and by varying their composition. The imaginary  $\epsilon''$  part of the complex permittivity of the thin films has a maximum due to the transverse oscillations of free electrons in the range of 1 eV to 3.5 eV. The films' applicability as amplifying substrates in surface-enhanced fluorescence was tested. Tryptophan and Cu (II)-phthalocyanine (CuPc) dye were used to analyze the efficiency of the localized surface plasmon resonance excitation in the ultraviolet spectral region. Amplification enhancing coefficient of 4.17 times was obtained in the case of CuPc dye.

Списание [J Physics: Conf Series 2240 \(2022\) 012007 \(1\)](#)

**31. Заглавие** Reversible supramolecular chiral structures induced in azopolymers by elliptically polarized light: influence of the irradiation wavelength and intensity

**Автори** B. Blagoeva, L. Nedelchev, D. Nazarova, E. Stoykova, J. Park

**Резюме** Photoinduced supramolecular chiral structures in azo materials have been extensively studied for the development of all-optical switches and because of their influence on the properties of certain types of polarization holographic gratings. Here, we investigate chiral structures induced by irradiation with elliptically polarized light in thin films of four azopolymers denoted as PAZO, P1, P1-2 which are amorphous, and P2 which is liquid crystalline. Their formation is characterized in real-time by the kinetics of azimuth rotation. The influence of the irradiation wavelength and intensity is also analyzed. The largest azimuth rotation per unit thickness is achieved in PAZO ( $33^\circ/\mu\text{m}$ ) and P1-2 ( $25^\circ/\mu\text{m}$ ). Reversibility of the chiral structures is demonstrated by a tenfold change in the direction of rotation. Our results also indicate that chiral structures formation occurs significantly faster than the induction of linear birefringence.

Списание [Appl Opt 61 \(5\) \(2022\) B147-B155](#)

**32. Заглавие** Composite thin films of azopolymer and embedded gold nanosized particles: evaluation of the effective complex refractive index

**Автори** N. Berberova-Buhova, P. Sharlandjiev, G. Mateev, L. Nedelchev, B. Blagoeva, E. Stoykova, D. Nazarova

**Резюме** Azobenzene and azobenzene-containing polymers are intensively studied because of their high potential for many novel applications in polarization holography, design of optical polarization-sensitive elements, optical storage, all-optical switching, diffractive optical elements, etc. We study in the paper a thin hybrid layer composed of a polymer matrix and embedded gold nanoparticles. For a polymer matrix we used polymer poly[1-[4-(3-carboxy4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt], denoted shortly as PAZO. Film reflectance and transmittance strongly depend on the morphology of nanoparticles and the composite film filling factor. Herein, we present essential details concerning the estimation of the film complex refractive index. The embedded particles are considered as ensemble of non-aggregated spheres with no multiple scattering by individual particles. The complex refractive index of the composite film is evaluated from the volume scattering efficiency of the Au particles, the PAZO matrix complex refractive index and the filling factor. Embedded Au spheres with ensemble mean diameters of 20, 60 and 100 nm are considered as well as filling factors of 0.008, 0.010 and 0.030.

**Списание** [J Chem Technol Metallurgy 57 \(2\) \(2022\) 241](#)

**33. Заглавие** Morphological evolution of thin AlN films grown by atomic layer deposition

**Автори** M. Beshkova, B. Blagoev, V. Mehandzhiev, R. Yakimova, B. Georgieva, I. Avramova, P. Terziyska, V. Strijkova

**Резюме** Thin AlN films were grown using a Beneq TFS-200 ALD reactor. TMA (trimethylaluminium) and NH<sub>3</sub> were used as precursors. The substrate temperature was 330 °C, the ALD cycles, 550. The TMA and NH<sub>3</sub> doses (pulses) lasted 180 ms and 90 ms, followed by 2-s and 9-s nitrogen gas purge, respectively. In order to study the morphological evolution of the thin AlN films, substrates providing different surface kinetics were used: Si-face and Cface of 4°-off axis and on-axis 4H-SiC, and graphene grown on 4H-SiC by sublimation. As revealed by atomic force microscopy (AFM), the lowest RMS surface roughness of about 0.8 nm was exhibited by the AlN film deposited on Si-face on-axis 4H-SiC due to its higher surface energy which provides for better film nucleation. The chemical composition and bonding states were investigated by X-ray photoelectron spectroscopy (XPS). The existence of AlN is justified by the presence of the XPS peaks of Al 2p and N 1s at about 73.3 eV and 396.6 eV, respectively.

These results are promising in view of further studies of thin AlN films properties for application in surface acoustic wave devices (SAW).

Списание [J Physics: Conf Series 2240 \(2022\) 012005 \(1\)](#)

### **34. Заглавие** Morphometry and Stiffness of Red Blood Cells—Signatures of Neurodegenerative Diseases and Aging

**Автори** V. Strijkova-Kenderova, S. Todinova, T. Andreeva, D. Bogdanova, A. Langari, A. Danailova, S. Krumova, E. Zlatareva, N. Kalaydzhiev, I. Milanov

**Резюме** Human red blood cells (RBCs) are unique cells with the remarkable ability to deform, which is crucial for their oxygen transport function, and which can be significantly altered under pathophysiological conditions. Here we performed ultrastructural analysis of RBCs as a peripheral cell model, looking for specific signatures of the neurodegenerative pathologies (NDDs)—Parkinson’s disease (PD), amyotrophic lateral sclerosis (ALS) and Alzheimer’s disease (AD), utilizing atomic force (AFM) and conventional optical (OM) microscopy. We found significant differences in the morphology and stiffness of RBCs isolated from patients with the selected NDDs and those from healthy individuals. Neurodegenerative pathologies’ RBCs are characterized by a reduced abundance of biconcave discoid shape, lower surface roughness and a higher Young’s modulus, compared to healthy cells. Although reduced, the biconcave is still the predominant shape in ALS and AD cells, while the morphology of PD is dominated by crenate cells. The features of RBCs underwent a marked aging-induced transformation, which followed different aging pathways for NDDs and normal healthy states. It was found that the diameter, height and volume of the different cell shape types have different values for NDDs and healthy cells. Common and specific morphological signatures of the NDDs were identified.

Списание [Int J Molec Sci 23 \(2022\) 227 \(1\)](#)

### **35. Заглавие** Morphometric and Nanomechanical Features of Erythrocytes Characteristic of Early Pregnancy Loss

**Автори** A. Langari, V. Strijkova, R. Komsa-Penkova, A. Danailova, S. Krumova, S. Taneva, I. Giosheva, E. Gartchev, K. Kercheva, A. Savov, S. Todinova

**Резюме** Early pregnancy loss (EPL) is estimated to be between 15 and 20% of all adverse pregnancies. Approximately, half of EPL cases have no identifiable cause. Herein, we apply atomic force microscopy to evaluate the alteration of morphology and nanomechanics of erythrocytes from women with EPL with unknown etiology, as compared to healthy pregnant (PC) and nonpregnant women (NPC). Freshly isolated erythrocytes from women with EPL

differ in both the roughness value ( $4.6 \pm 0.3$  nm,  $p < 0.05$ ), and Young's modulus ( $2.54 \pm 0.6$  MPa,  $p < 0.01$ ) compared to the values for NPC ( $3.8 \pm 0.4$  nm and  $0.94 \pm 0.2$  MPa, respectively) and PC ( $3.3 \pm 0.2$  nm and  $1.12 \pm 0.3$  MPa, respectively). Moreover, we find a time-dependent trend for the reduction of the cells' morphometric parameters (cells size and surface roughness) and the membrane elasticity— much faster for EPL than for the two control groups. The accelerated aging of EPL erythrocytes is expressed in faster morphological shape transformation and earlier occurrence of spiculated and spherical-shaped cells, reduced membrane roughness and elasticity with aging evolution. Oxidative stress in vitro contributed to the morphological cells' changes observed for EPL senescent erythrocytes. The ultrastructural characteristics of cells derived from women with miscarriages show potential as a supplementary mark for a pathological state.

**Списание** [Int J Molec Sci 23 \(2022\) 4512 \(91\)](#)

### **36. Заглавие** Reaction Kinetics and Mechanism of VOCs Combustion on Mn-Ce-SBA-15

**Автори** A. Naydenov, R. Velinova, J-L. Blin, L. Michelin, B. Lebeau, H. Kolev, Y. Karakirova, D. Karashanova, L. Vidal, A. Dotzeva, K. Tenchev, S. Todorova

**Резюме** A propane combustion catalyst based on Mn and Ce and supported by SBA-15 was prepared by the “two-solvents” method aiming at the possible application in catalytic converters for abatement of alkanes in waste (exhaust) gases. The catalyst characterization was carried out by SAXS, N<sub>2</sub>-physisorption, XRD, TEM, XPS, EPR and H<sub>2</sub>-TPR methods. The catalysts' performance was evaluated by tests on the combustion of methane, propane and butane. The reaction kinetics investigation showed that the reaction orders towards propane and oxygen were 0.7 and 0.1, respectively. The negative reaction order towards the water (−0.3) shows an inhibiting effect on the water molecules. Based on the data from the instrumental methods, catalytic experiments and mathematic modeling of the reaction kinetics, one may conclude that the Mars–van Krevelen type of mechanism is the most probable for the reaction of complete propane oxidation over single Mn and bi-component Mn-Ce catalysts. The fine dispersion of manganese and cerium oxide and their strong interaction inside the channels of the SBA-15 molecular sieve leads to the formation of difficult to reduce oxide phases and consequently, to lower catalytic activity compared to the mono-component manganese oxide catalyst. It was confirmed that the meso-structure was not modified during the catalytic reaction, thus it can prevent the agglomeration of the oxide particles.

**Списание** [Catalysts 12 \(6\) \(2022\) 583 \(1\)](#)

### **37. Заглавие** Platelets' Nanomechanics and Morphology in Neurodegenerative Pathologies

**Автори** V. Strijkova, S. Todinova, T. Andreeva, A. Langari, D. Bogdanova, E. Zlatareva, N. Kalaydzhiev, I. Milanov, S. Taneva

**Резюме** The imaging and force–distance curve modes of atomic force microscopy (AFM) are explored to compare the morphological and mechanical signatures of platelets from patients diagnosed with classical neurodegenerative diseases (NDDs) and healthy individuals. Our data demonstrate the potential of AFM to distinguish between the three NDDs—Parkinson’s disease (PD), amyotrophic lateral sclerosis (ALS) and Alzheimer’s disease (AD), and normal healthy platelets. The common features of platelets in the three pathologies are reduced membrane surface roughness, area and height, and enhanced nanomechanics in comparison with healthy cells. These changes might be related to general phenomena associated with reorganization in the platelet membrane morphology and cytoskeleton, a key factor for all platelets’ functions. Importantly, the platelets’ signatures are modified to a different extent in the three pathologies, most significant in ALS, less pronounced in PD and the least in AD platelets, which shows the specificity associated with each pathology. Moreover, different degree of activation, distinct pseudopodia and nanocluster formation characterize ALS, PD and AD platelets. The strongest alterations in the biophysical properties correlate with the highest activation of ALS platelets, which reflect the most significant changes in their nanoarchitecture. The specific platelet signatures that mark each of the studied pathologies can be added as novel biomarkers to the currently used diagnostic tools.

**Списание** [Biomedicines 10 \(2022\) 2239 \(1\)](#)

### **38. Заглавие** Effect of laser annealing on the properties of Ag/ZnO nanostructures

**Автори** M. Koleva, A. Dikovska, N. Nedyalkov, D. Karashanova

**Резюме** Ag/ZnO nanostructures were synthesized using pulsed laser deposition (PLD) in open air (at atmospheric pressure). The deposition was carried out by a Nd:YAG laser, with the Ag layer composed of nanoparticles grown on SiO<sub>2</sub> (001) substrates by the laser wavelength of 355 nm; this layer was covered by ZnO deposited by using the laser wavelength of 1064 nm. The samples were laser annealed, which led to a modification of the nanoparticles. The nanocomposites produced were characterized by TEM, UV–Vis and PL spectroscopy. The annealing procedures influence the optical properties of the Ag/ZnO nanocomposites. The laser annealing under certain parameters changes the emission behavior of the Ag/ZnO nanocomposite heterostructures. By employing localized surface plasmon resonance (LSPR), the near band edge (NBE) emission intensity of the ZnO films composed of nanoparticles was varied. An enhancement of the UV emission located at about 383 nm, commonly attributed to an excitonic transition, was registered after laser annealing with one pulse at the wavelength of 355 nm. The results obtained demonstrate that the annealing of Ag/ZnO composite nanostructures plays a key role in tuning the PL performance of a semiconductor material where an LSPR occurs.

**39. Заглавие** Gold-Based Catalysts for Complete Formaldehyde Oxidation: Insights into the Role of Support Composition

**Автори** L. Ilieva, D. Dimitrov, E. Kolentsova, A. Venezia, D. Karashanova, G. Avdeev, P. Petrova, R. State, T. Tabakova

**Резюме** Formaldehyde (HCHO) is recognized as one of the most emitted indoor air pollutants with high detrimental effect on human health. Significant research efforts are focused on HCHO removal to meet emission regulations in an effective and economically profitable way. For over three decades, the unique electronic properties and catalytic abilities of nano-gold catalysts continue to be an attractive research area for the catalytic community. Recently, we reported that mechanochemical mixing is a relevant approach to the preparation of Co-Ce mixed oxides with high activity in complete benzene oxidation. A trend of higher surface defectiveness, in particular, oxygen vacancies, caused by close interaction between cobalt oxide and cerium oxide phases, was observed for a mixed oxide composition of 70 wt.% Co<sub>3</sub>O<sub>4</sub> and 30 wt.% CeO<sub>2</sub>. These results directed further improvement by promotion with gold and optimization of mixed oxide composition, aiming for the development of an efficient catalyst for room temperature HCHO abatement. Support modification with potassium was studied; however, the K addition caused less enhancement of HCHO oxidation activity than expected. This motivated the preparation of new carrier material. In addition to Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> mixed metal oxides with preset ratio,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> intentionally containing 33% boehmite and shortly named Al<sub>2</sub>O<sub>3</sub>-b was used for synthesis. Analysis of the role of support composition in HCHO oxidation was based on the characterization of nano-gold catalysts by textural measurements, XRD, HRTEM, XPS, and TPR techniques. Gold supported on mechanochemically treated Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-b (50 wt.% Al<sub>2</sub>O<sub>3</sub>-b) exhibited superior activity owing to high Ce<sup>3+</sup> and Co<sup>3+</sup> surface amounts and the most abundant oxygen containing species with enhanced mobility. This catalyst achieved oxidation to CO<sub>2</sub> and H<sub>2</sub>O by 95% HCHO conversion at room temperature and 100% at 40 °C, thus implying the potential of this composition in developing efficient catalytic materials for indoor air purification.

**40. Заглавие** Novel Approach for Synthesis of Graphene-like Phases by Pulsed Laser Ablation in a Flow-Mode Suspension

**Автори** I. Avramova, D. Dimov, N. Stankova, M. Petrov, D. Karaivanova, G. Avdeev, S. Russev, D. Karashanova, B. Georgieva, E. Valcheva, T. Milenov

**Резюме** The present study investigates the possibility of obtaining graphene-like phases (defected graphene, graphene oxide, and reduced graphene oxide) as fine suspensions by applying a novel pulsed laser ablation (PLA) approach in flow mode. Two types of suspensions of microcrystalline graphite in aqueous suspensions and two types of microcrystalline graphite in suspensions of 6% hydrogen peroxide solution were irradiated in a quartz tube through which they flow. The third ( $\lambda = 355$  nm) and fourth harmonics ( $\lambda = 266$  nm) of an Nd:YAG laser system (15 ns pulse duration and 10 Hz pulse repetition rate) were used. The morphology of the obtained particles was studied by transmission electron microscopy (TEM). Their phase composition and structure were explored by X-ray photoelectron spectroscopy, X-ray diffractometry, and Raman spectroscopy.

**Списание** [Materials 15 \(22\) \(2022\) 7870 \(1\)](#)

**41. Заглавие** The Role of Alternative Electron Pathways for Effectiveness of Photosynthetic Performance of *Arabidopsis thaliana*, Wt and *lut2*, under Low Temperature and High Light Intensity

**Автори** A. Popova, M. Stefanov, A. Ivanov, M. Velitchkova

**Резюме** A recent investigation has suggested that the enhanced capacity for PSI-dependent cyclic electron flow (CEF) and PSI-dependent energy quenching that is related to chloroplast structural changes may explain the lower susceptibility of *lut2* to combined stresses—a low temperature and a high light intensity. The possible involvement of alternative electron transport pathways, proton gradient regulator 5 (PGR5)-dependent CEF and plastid terminal oxidase (PTOX)-mediated electron transfer to oxygen in the response of *Arabidopsis* plants—wild type (wt) and *lut2*—to treatment with these two stressors was assessed by using specific electron transport inhibitors. Re-reduction kinetics of  $P_{700}^+$  indicated that the capacity for CEF was higher in *lut2* when this was compared to wt. Exposure of wt plants to the stress conditions caused increased CEF and was accompanied by a substantial raise in PGR5 and PTOX quantities. In contrast, both PGR5 and PTOX levels decreased under the same stress conditions in *lut2*, and inhibiting PGR5-dependent pathway by AntA did not exhibit any significant effects on CEF during the stress treatment and recovery period. Electron microscopy observations demonstrated that under control conditions the degree of grana stacking was much lower in *lut2*, and it almost disappeared under the combined stresses, compared to wt. The role of differential responses of alternative electron transport pathways in the acclimation to the stress conditions that are studied is discussed.

**Списание** [Plants 11\(17\) \(2022\) 2318 \(1\)](#)

**42. Заглавие** Optical properties of the glasses from the system CaO-GeO<sub>2</sub>-Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> doped by terbium

**Автори** I. Koseva, V. Nikolov, M. Gancheva, L. Aleksandrov, P. Ivanov, P. Petrova, R. Iordanova, R. Tomova

**Резюме** Terbium doped glasses with three different compositions from the system CaO-GeO<sub>2</sub>-Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> and different dopant concentrations were prepared. DTA analyses show weak influence of the rare earth ion on the glass thermal properties. The FTIR spectra revealed variations between glass structures. Excitation and emission spectra of the doped glasses possess the characteristic transitions of Tb<sup>3+</sup> ions. Peaks locations are not dependent on the rare earth ion concentration and the glass composition, but some splitting appears. Chromaticity coordinates of Tb<sup>3+</sup> glasses are placed in a green and green-yellowish area of the color space diagram.

**Списание** [Mater Today: Proc 61 \(2022\) 1190](#)

**43. Заглавие** Rare earth concentration dependence on the glass optical properties in the system CaOAGeO<sub>2</sub>ALi<sub>2</sub>OAB<sub>2</sub>O<sub>3</sub> (RE = Dy<sup>3+</sup>)

**Автори** I. Koseva, V. Nikolov, M. Gancheva, L. Aleksandrov, P. Ivanov, P. Petrova, R. Iordanova, R. Tomova

**Резюме** Dy<sup>3+</sup> doped glasses from the oxide system CaOAGeO<sub>2</sub>ALi<sub>2</sub>OAB<sub>2</sub>O<sub>3</sub> with different compositions were prepared by melt quenching technique. The obtained glass samples were characterized by X-ray diffraction (XRD), Differential thermal analyses (DTA), Infrared spectroscopy (IR) and Photoluminescence (PL) measurements. The X-ray analysis reveals amorphous nature of the samples. Thermal stability of the doped glasses depends more on the glass composition than the dopant concentration. IR analyses confirm some changes in the local structures of the glasses after doping. The excitation and emission spectra show typical for Dy<sup>3+</sup> ions lines with domination of yellow emission peak. CIE coordinates and yellow-to-blue ratio of the obtained glasses is with almost the same values, therefore almost the same emitted color is expected.

**Списание** [Mater Today: Proc 61\(4\) \(2022\) 1249](#)

**44. Заглавие** Atomic layer deposition of AlN on different SiC surfaces

**Автори** M. Beshkova, P. Deminskyi, C-W. Hsu, I. Shtepliuk, I. Avramova, R. Yakimova, N. Pedersen

**Резюме** Thin AlN films were grown using a Picosun R-200 atomic layer deposition (ALD) reactor on SiC surfaces with different crystallographic orientation: on-axis 4H-SiC (0001) and 8° off-axis 4H-SiC. TMA (trimethylaluminium) and NH<sub>3</sub> were used as precursors while hydrogen and nitrogen plasma were applied for in-situ substrate cleaning. The substrate temperatures were 400 °C and 450 °C, with 20 ALD cycles. The surface morphology was investigated by scanning electron microscopy (SEM), which revealed nanometer-sized islands in all films. The AlN films deposited on on-axis 4H-SiC at 450 °C substrate temperature exhibited a relatively small roughness of about 0.255 nm. The chemical composition and bonding states were investigated by X-ray photoelectron spectroscopy. For all layers, high-resolution XPS showed Al 2p and N 1s spectra that are characteristic of AlN. These results are a good prerequisite of establishing the growth conditions of AlN films for surface acoustic wave (SAW) devices.

**Списание** [J Physics: Conf Series 2240 \(2022\) 012004](#)

**45. Заглавие** Structural and optical properties of MgMoO<sub>4</sub> prepared by mechanochemical technique

**Автори** M. Gancheva, T. Rojac, R. Iordanova, I. Piroeva, P. Ivanov

**Резюме** MgMoO<sub>4</sub> with hexagonal particles were prepared by combining high energy ball milling with heat treatment technique. The influence of the mechanochemical activation/heat-treatment on the phase, structural and morphology transformation were investigated by X-ray powder diffraction analysis (XRD), infrared spectroscopy (IR), differential scanning calorimetry (DSC), particle size distribution (PSD) and scanning electron microscope (SEM). Optical properties of the final product were studied by UV–Vis and photoluminescence (PL) measurements. Mechanochemical activation of the initial oxides for 10 h ball milling leads to a full amorphization of MoO<sub>3</sub>, only. The heat-treatment at different temperatures after 10 h milling time results to the phase formation of MgMoO<sub>4</sub>. The reaction started at 400 °C for 5 h and completed at 800 °C for 5 h. The calculated energy band gap value as prepared MgMoO<sub>4</sub> is 2.03 eV and exhibits photoluminescence emission above 600 nm. The CIE chromaticity coordinates ( $x = 0.53$  and  $y = 0.43$ ) were found to lie in the orange region.

**Списание** [Ceram Int 48 \(2022\) 17149](#)

**46. Заглавие** On the structures and luminescence properties of Eu<sup>3+</sup>-doped Li<sub>2</sub>CaGeO<sub>4</sub>, Ca<sub>2</sub>GeO<sub>4</sub>, and Ca<sub>5</sub>Ge<sub>3</sub>O<sub>11</sub> compounds

**Автори** I. Koseva, V. Nikolov, R. Nikolova, P. Tzvetkov, P. Ivanov, P. Petrova, R. Tomova, N. Kuvandjiev, M. Tarassov

**Резюме** Powder samples of  $\text{Li}_2\text{CaGeO}_4$ ,  $\text{Ca}_2\text{GeO}_4$ , and  $\text{Ca}_5\text{Ge}_3\text{O}_{11}$  doped by 0.5, 1, 2, 3, 4 and 5 at%  $\text{Eu}^{3+}$  relative to the  $\text{Ca}^{2+}$ , were prepared using a conventional solid-state synthesis technique. X-ray diffraction (XRD) analyses confirmed obtaining the pure phases at all dopant concentrations. In parallel, single crystals of the three compounds with the experimentally found optimal  $\text{Eu}^{3+}$  concentration were grown using a flux method. Structural investigation on the single crystals were done with a special attention to the form of the Ca–O polyhedron, the mean Ca–O distance, the Ca–Ca distance in the structure, the distortion degree of the polyhedron, as well as the Eu–Ca substitution site. The main spectral characteristics were analyzed and several relationships between the structural and spectra features were found. The optimal dopant concentration was 3 at% for  $\text{Ca}_2\text{GeO}_4$  and 4at% for  $\text{Ca}_5\text{Ge}_3\text{O}_{11}$  and  $\text{Li}_2\text{CaGeO}_4$ . Commission Internationale de l'éclairage coordinates of the samples showed emission colours in the red region close to the standard red coordinates and slightly influenced by the active ion concentration. The obtained results showed that europium-doped  $\text{Li}_2\text{CaGeO}_4$ ,  $\text{Ca}_2\text{GeO}_4$ , and  $\text{Ca}_5\text{Ge}_3\text{O}_{11}$  could be used as red phosphors.

**Списание** [Luminescence 37 \(2022\) 1492](#)

**47. Заглавие** Strong increase the photoluminescence of  $\text{Dy}^{3+}$  doped germanate compounds by optimizing the synthesis conditions

**Автори** I. Koseva, V. Nikolov, P. Tzvetkov, P. Ivanov, D. Karashanova

**Резюме** The aim of the present study was to investigate the influence of synthesis conditions (temperature and synthesis time) and consequently the change in particle size and shape, their size distribution, degree of agglomeration and the degree of crystallinity on the emission intensity of three different germanates  $\text{Li}_2\text{CaGeO}_4$ ,  $\text{Ca}_2\text{GeO}_4$  and  $\text{Ca}_5\text{Ge}_3\text{O}_{11}$  doped by 1 at%  $\text{Dy}^{3+}$ . The analysis showed that the emission intensities of  $\text{Li}_2\text{CaGeO}_4$ ,  $\text{Ca}_2\text{GeO}_4$  and  $\text{Ca}_5\text{Ge}_3\text{O}_{11}$  doped by 1 at%  $\text{Dy}^{3+}$  increase 4, 10 and 3 times only as a result of optimizing the synthesis conditions. Studies have shown definitely that the dominant factor for this strong increase of the emission intensity is the increase of the degree of crystallinity. The presence of agglomeration in high temperature synthesis (in the case of  $\text{Ca}_2\text{GeO}_4$ ) strongly reduces the emission intensity. The sizes and shape of the particles, as well as their size distribution for the three investigated compounds are of secondary importance for the emission intensity

**Списание** [Mater Today Commun 33 \(2022\) 104601](#)

**47. Заглавие** Photocatalytic activation of  $\text{TiO}_2$ -functionalized anodic aluminium oxide for electroless copper deposition

**Автори** B. Stefanov, V. Milusheva, H. Kolev, B. Tzaneva

**Резюме** Herein, we demonstrate conductive copper layer patterning of a  $\text{TiO}_2$ -functionalized anodic aluminium oxide (AAO) surface by Cu electroless deposition (Cu-ELD). 4  $\mu\text{m}$  thick

AAO layers were obtained by anodization of Al foil at 140 V in 5% H<sub>3</sub>PO<sub>4</sub> and then surface-functionalized with TiO<sub>2</sub> via sol-gel dip-coating. The TiO<sub>2</sub>/AAO composites exhibited a dissolution rate 48% lower than that of AAO at pH 12.8, allowing their metalization in alkaline, HCHO-based, Cu electroless deposition bath. In lieu of a noble-metal catalyst, spatially-selective surface activation of TiO<sub>2</sub>/AAO was accomplished by photocatalytic reduction of Cu[EDTA] complex under UV LED illumination through a photomask, at a varied UV dose (1.25 – 20 J cm<sup>-2</sup>). Uniform TiO<sub>2</sub>/AAO surface coverage with Cu[EDTA] reduction products was obtained at doses ≤ 7.5 J cm<sup>-2</sup>, followed by the formation of particles (100 – 500 nm diameter) upon prolonged UV exposure. XPS analysis revealed a mixed phase Cu<sup>+</sup>:Cu<sup>2+</sup> composition in 3:1 ratio, of the as-deposited Cu-particles, which were able to successfully activate electroless Cu deposition. Conductive copper patterns with sheet resistance as low as 0.54 Ω/sq. were obtained after 15 min in the Cu-ELD bath.

Списание [Catal Sci Technol 12 \(2022\) 7027](#)

**49. Заглавие** Preferential CO oxidation in hydrogen-rich gases over Ag catalysts supported on different supports

**Автори** S. Todorova, H. Kolev, Y Karakirova, D. Filkova, B. Grahovski, K. Aleksieva, J. Holdago, G. Kadinov, A. Caballero

**Резюме** The monometallic silver supported on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZSM-5 (Si:Al=100) and bimetallic AgCe/SiO<sub>2</sub> samples were studied in the reaction of the preferential CO oxidation. It was established that the supported silver catalysts are promising systems for selective oxidation of CO at low temperatures and the addition of cerium oxide increases the catalytic activity and selectivity most probably because of the increase in the silver dispersion; the homogeneous distribution of Ag and ceria on the silica support; formation of Ag<sup>n</sup> δ<sup>+</sup> clusters; increase in bulk and subsurface oxygen.

Списание [Reac Kinet Mech Cat 135 \(2022\) 1405](#)

**50. Заглавие** Reaction kinetics and mechanism of the catalytic oxidation of propane over Co–ZSM-5 zeolites

**Автори** R. Velinova, B. Grahovski, H. Kolev, G. Ivanov, S. Todorova, A. Naydenov

**Резюме** The complete oxidation of propane over Co-containing ZSM-5 zeolites having different Si/Al ratios (23, 40 and 100) was studied. It was observed that the applied preparation procedure ensured a fine dispersion of Co<sub>3</sub>O<sub>4</sub>. Regarding the surface composition, both

$\text{Co}^{2+}$  and  $\text{Co}^{3+}$  were present on the surface. The oxo cations containing  $\text{Co}^{2+}$  and/or  $\text{CoO}_x$  stabilized inside the zeolite and  $\text{Co}^{2+}$  ions at the exchange sites are also formed. It was found out that the complete oxidation of propane proceeds at catalyst bed temperatures above 240 °C and the needed temperature to achieve 30% conversion of propane ( $T_{30}$ ) at gas hourly space velocity of 100,000  $\text{h}^{-1}$  is 314–338 °C. The high catalytic activity of Co–ZSM-5 ( $\text{Si}/\text{Al} = 23$ ) is explained by the high reducibility as result of lower interaction of the cobalt oxide with the support. Based on the study of the reaction kinetics, the mechanism of Mars–van Krevelen was considered to be the most probable. Based on the observed activity of the prepared Co–ZSM-5 materials, one could expect further development of these new catalytic systems for real application in the reduction of greenhouse gas emissions.

Списание [Reac Kinet Mech Cat 135 \(2022\) 83](#)

### **51. Заглавие** Catalytic combustion of methane over Ni modified Pd/Al<sub>2</sub>O<sub>3</sub> catalysts

**Автори** S. Todorova, A. Naydenov, R. Velinova, H. Kolev, A. Larin, D. Karashanova

**Резюме** New data on the catalytic combustion of methane on Ni modified Pd/Al<sub>2</sub>O<sub>3</sub> catalysts were obtained. NiAl<sub>2</sub>O<sub>4</sub> spinel phase, not well definite Ni-Al phases, reducible at lower temperatures as well as finely dispersed NiO are formed on the surface after Ni deposition. When Pd is loaded on alumina modified with up to 5% Ni, the finely divided not well stabilized PdO particles are formed. PdO strongly interacting with surface is formed in Pd + 10% Ni/Al<sub>2</sub>O<sub>3</sub>. All three oxidation states Pd<sup>0</sup>, Pd<sup>2+</sup> and Pd<sup>4+</sup> are registered on the surface of the studied catalysts. The observed close catalytic activity of all nickel-modified catalysts is explained by the similar surface palladium concentration, which indicates that increasing the nickel content does not lead to a significant improvement in catalytic activity.

Списание [Mater Today: Proc 61 \(2022\) 1212](#)

### **52. Заглавие** Comparative Corrosion Characterization of Hybrid Zinc Coatings in Cl<sup>-</sup>-Containing Medium and Artificial Sea Water

**Автори** N. Boshkova, K. Kamburova, T. Radeva, S. Simeonova, N. Grozev, M. Shipochka, N. Boshkov

**Резюме** The presented investigations demonstrate the corrosion behavior and protective ability of hybrid zinc coatings specially designed for combined protection of low-carbon steel from localized corrosion and biofouling. Polymer-modified copper oxide (CuO) nanoparticles as widely used classic biocide are applied for this purpose, being simultaneously electrodeposited with zinc from electrolytic bath. The corrosion behavior of the hybrid coatings is evaluated in a model corrosive medium of 5% NaCl solution and in artificial sea water (ASW). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to characterize the

surface morphology of pure and hybrid zinc coatings. Contact angle measurements are realized with an aim to determine the hydrophobicity of the surface. X-ray photoelectron spectroscopy (XPS) is applied for evaluation of the chemical composition of the surface products appearing as a result of the corrosion treatment. Potentiodynamic polarization (PDP) curves and polarization resistance ( $R_p$ ) measurements are used to estimate the protective characteristics in both model corrosive media. The results obtained for the hybrid coatings are compared with the corrosion characteristics of ordinary zinc coating with the same thickness. It was found that the hybrid coating improves the anticorrosion behavior of low-carbon steel during the time interval of 35 days and at conditions of external polarization. The tests demonstrate much larger corrosion resistance of the hybrid coating in ASW compared to 5% NaCl solution. The obtained results indicated that the proposed hybrid zinc coating has a potential for antifouling application in marine environment.

Списание [Coatings 12\(12\) \(2022\) 1798](#)

### **53. Заглавие** Hydrodeoxygenation of Levulinic Acid to $\gamma$ -Valerolactone over Mesoporous Silica-Supported Cu-Ni Composite Catalysts

**Автори** М. Popova, I. Trendafilova, M. Oykova, Y. Mitrev, P. Shestakova, M. Mihályi, Á. Szegedi

**Резюме** Monometallic (Cu, Ni) and bimetallic (Cu-Ni) catalysts supported on KIT-6 based mesoporous silica/zeolite composites were prepared using the wet impregnation method. The catalysts were characterized using X-ray powder diffraction,  $N_2$  physisorption, SEM, solid state NMR and  $H_2$ -TPR methods. Finely dispersed NiO and CuO were detected after the decomposition of impregnating salt on the silica carrier. The formation of small fractions of ionic  $Ni^{2+}$  and/or  $Cu^{2+}$  species, interacting strongly with the silica supports, was found. The catalysts were studied in the gas-phase upgrading of lignocellulosic biomass-derived levulinic acid (LA) to  $\gamma$ -valerolactone (GVL). The bimetallic, CuNi-KIT-6 catalyst showed 100% LA conversion at 250 °C and atmospheric pressure. The high LA conversion and GVL yield can be attributed to the high specific surface area and finely dispersed Cu-Ni species in the catalyst. Furthermore, the catalyst also exhibited high stability after 24 h of reaction time with a GVL yield above 80% without any significant change in metal dispersion.

Списание [Molecules 27 \(2022\) 5383](#)

### **54. Заглавие** Bioinspired Remineralization of Artificial Caries Lesions Using PDMAEMA/Carbomer/Calcium Phosphates Hybrid Microgels

**Автори** А. Bonchev, M. Simeonov, P. Shestakova, R. Vasileva, R. Titorenkova, A. Apostolov, E. Dyulgerova, E. Vassileva

**Резюме** Dental caries remains one of the most prevalent bacterium-caused chronic diseases affecting both adults and children worldwide. The development of new materials for enhancing its remineralization is one of the most promising approaches in the field of advanced dental materials as well as one of the main challenges in non-invasive dentistry. The aim of the present study is to develop novel hybrid materials based on (PDMAEMA)/Carbomer 940 microgels with in situ deposited calcium phosphates (CaP) and to reveal their potential as a remineralization system for artificial caries lesions. To this purpose, novel PDMAEMA/Carbomer 940 microgels were obtained and their core-shell structure was revealed by transmission electron microscopy (TEM). They were successfully used as a matrix for in situ calcium phosphate deposition, thus giving rise to novel hybrid microgels. The calcium phosphate phases formed during the deposition process were studied by X-ray diffraction and infrared spectroscopy, however, due to their highly amorphous nature, the nuclear magnetic resonance (NMR) was the method that was able to provide reliable information about the formed inorganic phases. The novel hybrid microgels were used for remineralization of artificial caries lesions in order to prove their ability to initiate their remineralization. The remineralization process was followed by scanning electron microscopy (SEM), X-ray diffraction, infrared and Raman spectroscopies and all these methods confirmed the successful enamel rod remineralization upon the novel hybrid microgel application. Thus, the study confirmed that novel hybrid microgels, which could ensure a constant supply of calcium and phosphate ions, are a viable solution for early caries treatment.

**Списание** [Gels 8 \(2022\) 681](#)

## **55. Заглавие** Mononuclear copper(II) complexes of the macrolide antibiotics tylosin and tilmicosin

**Автори** I. Pantcheva, R. Stambolyiska, N. Petkov, A. Tadjer, S. Simova, R. Stoyanova, R. Kukleva, P. Dorkov

**Резюме** The 16-membered macrolide antibiotics tylosin (HTyl) and tilmicosin (HTilm) react with Cu(II) to form isostructural mononuclear complexes of composition  $[\text{CuL}_2]$  ( $\text{L} = \text{Tyl}^-$  (**1**),  $\text{Tilm}^-$  (**2**)). Reactions take place in aqueous alkaline solutions, at molar metal-to-ligand ratio ranging from 1:10 to 1:2. The coordination species obtained were characterized by physico-chemical and spectroscopic methods. Experimental data and quantum chemical calculations revealed that the copper atom is placed in a square-planar environment and the main chromophore unit is of composition  $[\text{CuN}_2\text{O}_2]$ . The complexes consist of two ligand monoanions acting in a bidentate coordination mode via the tertiary nitrogen atom and the deprotonated hydroxyl group of the mycaminosyl substituent. The antibacterial assay of the macrolides and their mononuclear copper(II) complexes **1–2** against Gram-positive microorganisms demonstrated that the new coordination compound of tilmicosin exhibits enhanced activity compared to that of the parent ligand.

**56. Заглавие** Antimicrobial Triterpenoids and Ingol Diterpenes from Propolis of Semi-Arid Region of Morocco

**Автори** R. Chimshirova, M. Popova, A. Chakir, V. Valcheva, S. Dimitrov, B. Trusheva, A. Romane, V. Bankova

**Резюме** The chemical composition and antimicrobial activity of propolis from a semi-arid region of Morocco were investigated. Fifteen compounds, including triterpenoids (**1**, **2**, **7–12**), macrocyclic diterpenes of ingol type (**3–6**) and aromatic derivatives (**13–15**), were isolated by various chromatographic methods. Their structures were elucidated by a combination of spectroscopic and chiroptical methods. Compounds **1** and **3** are new natural compounds, and **2**, **4–6**, and **9–11** are newly isolated from propolis. Moreover, the full nuclear magnetic resonance (NMR) assignments of three of the known compounds (**2**, **4** and **5**) were reported for the first time. Most of the compounds tested, especially the diterpenes **3**, **4**, and **6**, exhibited very good activity against different strains of bacteria and fungi. Compound **3** showed the strongest activity with minimum inhibitory concentrations (MICs) in the range of 4–64 µg/mL. The combination of isolated triterpenoids and ingol diterpenes was found to be characteristic for *Euphorbia* spp., and *Euphorbia officinarum* subsp. *echinus* could be suggested as a probable and new plant source of propolis.

**57. Заглавие** Fabrication of electrospun cellulose acetate/nanoclay composites for pollutant removal

**Автори** P. Tsekova, O. Stoilova

**Резюме** The creation of eco-friendly clay-based composites for pollutant removal by adsorption still remains a challenge. This problem might be successfully solved by the development of electrospun polymer–clay composites. For the first time in this study, a one-step fabrication of cellulose acetate (CA) fibers filled with commercially available nanoclays (NCs) was described. The optimal ratio at which CA/NCs dispersions remained stable was accomplished by varying the nanoclay concentration with respect to CA. Furthermore, the selected solvent system and the electrospinning conditions allowed for the successful fabrication of electrospun CA/NC composites. It was found that the composites' surface morphology was not affected by the incorporated nanoclays and was the same as that of the electrospun CA fibers. The performed analyses clearly showed that CA and nanoclays did not react during the electrospinning process. It was found that the distribution of nanoclay layers

probably was a mixture of intercalated and exfoliated structures. Notably, the type of the nanoclay strongly influenced the adsorption ability of CA/NC composites toward Cr(VI) ions and MB dye. These results suggested that the fabricated CA/NC composites are suitable for pollutant removal due to their specific structure.

Списание [Polymers 14 \(2022\) 5070](#)

**58. Заглавие** Bio-based Electrospun Fibers from Chitosan Schiff Base and Polylactide and Their Cu<sup>2+</sup> and Fe<sup>3+</sup> Complexes: Preparation and Antibacterial and Anticancer Activities

**Автори** М. Ignatova, I. Anastasova, N. Manolova, I. Rashkov, N. Markova, R. Kukeva, R. Stoyanova, A. Georgieva, R. Toshkova

**Резюме** The Schiff base derivative (Ch-8Q) of chitosan (Ch) and 8-hydroxyquinoline-2-carboxaldehyde (8QCHO) was prepared and fibrous mats were obtained by the electrospinning of Ch-8Q/polylactide (PLA) blend solutions in trifluoroacetic acid (TFA). Complexes of the mats were prepared by immersing them in a solution of CuCl<sub>2</sub> or FeCl<sub>3</sub>. Electron paramagnetic resonance (EPR) analysis was performed to examine the complexation of Cu<sup>2+</sup>(Fe<sup>3+</sup>) in the Ch-8Q/PLA mats complexes. The morphology of the novel materials and their surface chemical composition were studied by scanning electron microscopy (SEM), attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). The performed microbiological screening demonstrated that in contrast to the neat PLA mats, the Ch-8Q-containing mats and their complexes were able to kill all *S. aureus* bacteria within 3 h of contact. These fibrous materials had efficiency in suppressing the adhesion of pathogenic bacteria *S. aureus*. In addition, Ch-8Q/PLA mats and their complexes exerted good anticancer efficacy in vitro against human cervical HeLa cells and human breast MCF-7 cells. The Ch-8Q-containing fibrous materials had no cytotoxicity against non-cancer BALB/c 3T3 mouse fibroblast cells. These properties render the prepared materials promising as wound dressings as well as for application in local cancer treatment.

Списание [Polymers 14 \(2022\) 5002](#)

**59. Заглавие** Redox-Responsive Crosslinked Mixed Micelles for Controllable Release of Caffeic Acid Phenethyl Ester

**Автори** К. Kamenova, G. Grancharov, V. Kortenova, P. Petrov

**Резюме** We report the elaboration of redox-responsive functional micellar nanocarriers designed for triggered release of caffeic acid phenethyl ester (CAPE) in cancer therapy. Three-layered micelles, comprising a poly( $\epsilon$ -caprolactone) (PCL) core, a middle poly(acrylic acid)/poly(ethylene oxide) (PAA/PEO) layer and a PEO outer corona, were prepared by co-

assembly of PEO<sub>113</sub>-*b*-PCL<sub>35</sub>-*b*-PEO<sub>113</sub> and PAA<sub>13</sub>-*b*-PCL<sub>35</sub>-*b*-PAA<sub>13</sub> amphiphilic triblock copolymers in aqueous media. The preformed micelles were loaded with CAPE via hydrophobic interactions between the drug molecules and PCL core, and subsequently crosslinked by reaction of carboxyl groups from PAA and a disulfide crosslinking agent. The reaction of crosslinking took place in the middle layer of the nanocarriers without changing the encapsulation efficiency (EE~90%) of the system. The crosslinked polymeric micelles (CPMs) exhibited superior structural stability and did not release CAPE in phosphate buffer (pH 7.4). However, in weak acidic media and in the presence of 10 mM reducing agent (dithiothreitol, DTT), the payload was released at a high rate from CPMs due to the breakup of disulfide linkages. The physicochemical properties of the nanocarriers were investigated by dynamic and electrophoretic light scattering (DLS and ELS) and atomic force microscopy (AFM). The rapid release of CAPE under intracellular-like conditions and the lack of premature drug release in media resembling the blood stream (neutral pH) make the developed CPMs a promising candidate for controllable drug release in the microenvironment of tumors.

Списание [Pharmaceutics 14\(3\) \(2022\) 679](#)

## **60. Заглавие** Functional Nanogel from Natural Substances for Delivery of Doxorubicin

**Автори** K. Kamenova, L. Radeva, K. Yoncheva, F. Ublekov, M. Ravutsov, M. Marinova, S. Simeonov, A. Forys, B. Trzebicka, P. Petrov

**Резюме** Nanogels (NGs) have attracted great attention because of their outstanding biocompatibility, biodegradability, very low toxicity, flexibility, and softness. NGs are characterized with a low and nonspecific interaction with blood proteins, meaning that they do not induce any immunological responses in the body. Due to these properties, NGs are considered promising candidates for pharmaceutical and biomedical application. In this work, we introduce the development of novel functional nanogel obtained from two naturally based products—citric acid (CA) and pentane-1,2,5-triol (PT). The nanogel was synthesized by precipitation esterification reaction of CA and PT in tetrahydrofuran using N-ethyl-N'-(3-dimethylaminopropyl) carbodiimide (EDC) and 4-(dimethylamino)pyridine (DMAP) catalyst system. Dynamic light scattering (DLS), cryogenic transmission electron microscopy (cryo-TEM) and atomic force microscopy (AFM) analyses revealed formation of spherical nanogel particles with a negative surface charge. Next, the nanogel was loaded with doxorubicin hydrochloride (DOX) by electrostatic interactions between carboxylic groups present in the nanogel and amino groups of DOX. The drug-loaded nanogel exhibited high encapsulation efficiency (EE~95%), and a bi-phasic release behavior. Embedding DOX into nanogel also stabilized the drug against photodegradation. The degradability of nanogel under acidic and neutral conditions with time was investigated as well.

Списание [Polymers 14 \(2022\) 3694](#)

**61. Заглавие** Nucleic acid-based supramolecular structures: vesicular spherical nucleic acids from a non-phospholipid nucleolipid

**Автори** E. Dimitrov, N. Toncheva-Moncheva, P. Bakardzhiev, A. Forsys, J. Doumanov, K. Mladenova, S. Petrova, B. Trzebicka, S. Rangelov

**Резюме** Vesicular spherical nucleic acids are dynamic nucleic acid-based supramolecular structures that are held together *via* non-covalent bonds. They have promising applications as drug and nucleic acid delivery materials, diagnostic and imaging tools and platforms for development of various therapeutic schemes. In this contribution, we report on vesicular spherical nucleic acids, constructed from a non-phospholipid nucleolipid – an original hybrid biomacromolecule, composed of a hydrophobic residue, resembling that of the naturally occurring phospholipids, and a DNA oligonucleotide strand. The nucleolipid was synthesized by coupling of dibenzocyclooctyne-functionalized oligonucleotide and azidated 1,3-dihexadecyloxy-propane-2-ol *via* an azide–alkyne *click* reaction. In aqueous solution it spontaneously self-associated into nanosized supramolecular structures, identified as unilamellar vesicles composed of a self-closed *interdigitated* bilayer. Vesicular structures were also formed upon intercalation of the nucleolipid *via* its lipid-mimetic residue in the phospholipid bilayer membrane of liposomes prepared from readily available and FDA-approved lipids (1,2-dipalmitoyl-*rac*-glycero-3-phosphocholine and cholesterol). The vesicular structures are thoroughly investigated by light scattering (dynamic, static, and electrophoretic) and cryogenic TEM and the physical characteristics, in particular, number of strands per particle, grafting density, and conformation of the strands, were compared to those of reference spherical nucleic acids. Finally, the vesicular structures were shown to exhibit cellular internalization with no need of transfection agents and enhanced colloidal and nuclease stability.

**Списание** [Nanoscale Adv 4\(18\) \(2022\) 3793](#)

**62. Заглавие** Quercetin- and Rutin-Containing Electrospun Cellulose Acetate and Polyethylene Glycol Fibers with Antioxidant and Anticancer Properties

**Автори** N. Stoyanova, M. Spasova, N. Manolova, I. Rashkov, A. Georgieva, R. Toshkova

**Резюме** Innovative fibrous materials from cellulose derivative, cellulose acetate (CA) and water-soluble polyether, polyethylene glycol (PEG) loaded with natural biologically active compounds (BAC), quercetin (QUE) and rutin (RUT), have been successfully fabricated by blend electrospinning and dual electrospinning. Scanning electron microscopy revealed that the mean fiber diameters of all the obtained fibers were in the nanometer range. QUE and RUT incorporated in the fibrous mats were in the amorphous state, as evidenced by the performed differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis. The presence of

the polyether in the developed fibrous material assisted the in vitro release of the biologically active compounds by improving the hydrophilicity and wettability of the mats. Rutin-containing fibrous materials manifest the highest antioxidative activity, as determined by the 2,2-diphenyl-1-picryl-hydrazyl-hydrate free radical method. The cytotoxicity of the fabricated novel materials was evaluated using a tumor cell line and normal mouse fibroblast cells. The mats containing QUE and QUE/RUT independent of the applied spinning method show a higher cytotoxic effect against cancer cells and 3 to 4.5 times lower cytotoxicity to a noncancer cell line. These features make the quercetin- and rutin-containing fibrous materials promising candidates for pharmaceutical, cosmetic, and biomedical use.

Списание [Polymers 14 \(2022\) 5380](#)

### **63. Заглавие** Nanoarchitectonics of Spherical Nucleic Acids with Biodegradable Polymer Cores: Synthesis and Evaluation

**Автори** R. Kalinova, K. Mladenova, S. Petrova, J. Doumanov, I. Dimitrov

**Резюме** Spherical nucleic acids (SNAs) have gained significant attention due to their unique properties allowing them to overcome the challenges that face current nanocarriers used for gene therapies. The aim of this study is to synthesize and characterize polymer–oligonucleotide conjugates of different architecture and to evaluate the possibility of forming SNAs with biodegradable cores. Initially, two types of azide (multi)functional polyester-based (co)polymers were successfully synthesized and characterized. In the next step, short oligonucleotide strands were attached to the polymer chains applying the highly efficient and metal-free “click” reaction, thus forming conjugates with block or graft architecture. Both conjugates spontaneously self-assembled in aqueous media forming nanosized SNAs with a biodegradable polyester core and a surface of oligonucleotide chains as evidenced from dynamic and electrophoretic light scattering measurements. The nano-assemblies were in vitro evaluated for potential cytotoxicity. Furthermore, the interactions of the newly synthesized SNAs with membrane lipids were studied. The preliminary results indicate that both types of polymer-based SNAs are good candidates for potential application in gene therapy and that it is worth to be further evaluated.

Списание [Materials 15 \(2022\) 8917](#)

### **64. Заглавие** 2D Monte Carlo Simulation of Cocrystal Formation Using Patchy Particles

**Автори** B. Rangelov, Ch. Nanev

**Резюме** Cocrystals of Active Pharmaceutical Ingredients (APIs) are an attractive therapeutic alternative to salt formations. However, due to the molecular scale processes involved, the

earliest stages of cocrystal formation remain poorly understood. In this paper, some light is shed on the thermodynamics and kinetics of co-crystallization. Importantly, to mimic the molecular scale processes of cocrystal formation, we use 2D Monte Carlo simulations and a computational model with short-range attraction and a mixture of two types of patchy particles (PPs) monomers. Each type possesses four patches, grouped in two by two, and each couple of patches is characterized by its specific placement on the circumference of the monomer and corresponding patch strength (a strong and narrow or weak and wide interaction). The spatial placement of the patches on both PPs monomers (alternating periodically through 60 and 120 degrees and vice versa) selected by us shows the emergence of both rhombohedral (metastable) and trihexagonal (stable) Kagome-like structures. The Kagome-like structures are preceded by formation of two types of trimers involving strong bonds only, or mixed trimers of strong and weak bonds, the later serving as building blocks for the finally generated Kagome patchy cocrystal, after prolonged simulation times. The step-by step process governing the cocrystal formation is discussed in detail, concerning the temperature interval, concentrations of PPs, the specific patch geometry and patch anisotropy as well. It is to be hoped that an understanding of the mechanisms of co-crystallization can help to control practical cocrystal synthesis and the possible phase transformations.

**Списание** [Crystals 12 \(2022\) 1457](#)

**65. Заглавие** Electrocatalytic Properties of Electroless Ni–P Coatings Towards Hydrogen Evolution Reaction in Alkaline Solution: Ni–P Coatings Deposited on Steel Substrate at Different Concentrations of Sodium Hypophosphite

**Автори** V. Chakarova, M. Monev

**Резюме** The hydrogen evolution reaction on electroless Ni–P alloy coatings on steel substrate with decreasing content of P from 8.2 to 3.4 wt% is investigated in 1 M KOH. The lowering of the P content in the alloy coating is achieved by decreasing the concentration of sodium hypophosphite in the solution for electroless deposition. Electrochemical investigations in combination with electron microscopy and radiographic analyses (SEM, EDS, XRD, TEM) reveal that the electrocatalytic activity of Ni–P coatings in regard to the hydrogen evolution reaction depends on the complex action of structure (morphology, phase composition), P content, and thickness. A change in any of these characteristics may lead to a change in other properties such as ability of the electrodes to adsorb and absorb hydrogen. Correct assessment of the contribution of individual factors is not possible due to the fact that the conditions for obtaining the coatings cannot be set in such a way as to lead to a change in only one of the factors.

**66. Заглавие** Hybrid Zinc Coating with CuO Nanocontainers Containing Corrosion Inhibitor for Combined Protection of Mild Steel from Corrosion and Biofouling

Списание [Electrocatalysis 14 \(2023\) 259](#)

**Автори** К. Камбурова, N. Boshkova, N. Boshkov, Ts. Radeva

**Резюме** In this study, a multifunctional hybrid coating is designed for the combined protection of mild steel from corrosion and biofouling in aggressive salt water. This involves preparation of a pH-responsive-release system based on copper oxide (CuO) as a biocide, and the corrosion inhibitor Safranin loaded in polymeric nanocontainers by alternate adsorption of poly(acrylic acid) and poly(ethylenimine) on CuO nanoparticles in water solutions. By optimizing the conditions, i.e., pH and concentration, good stability of the suspensions and the loading amount of Safranin is achieved. The nanocontainers are electrodeposited as an intermediate layer in an ordinary zinc coating on steel (“sandwich-like” structure) from the water solution in order to minimize the effect of CuO dissolution. To highlight the role of Safranin in reducing steel corrosion, a second zinc coating containing CuO nanoparticles without a corrosion inhibitor is also examined. The surface morphology and corrosion behavior of the hybrid coatings are evaluated in a model corrosion medium (5% NaCl solution). Both coatings are found to improve the anticorrosion behavior of steel for a time interval of 55 days and at conditions of external polarization. It can be expected that the newly developed hybrid coatings would also demonstrate potential for marine applications due to the main characteristics of their components.

Списание [Coatings 12 \(2022\) 1254](#)

**67. Заглавие** Anion and radical anion products of flutamide studied by IR spectra and density functional calculations

**Автори** S. Stoyanov, D. Yancheva, E. Velcheva, B. Stamboliyska

**Резюме** Flutamide, antiandrogen drugs for prostate cancer, was studied by spectroscopic and DFT methods to estimate its ability to form anion and radical anion products. The azanion was generated in DMSO-d<sub>6</sub> solution by treatment with sodium methoxide and the resulting spectral changes were followed by IR spectroscopy. IR measurements in electrochemical solution cell were performed to characterize the reductive behavior of flutamide. The different conformers of flutamide, its anion and radical anions, the spectral changes expected related to the conversion into anionic species and several molecular parameters were computationally estimated based on DFT. The structure, electronic charge and spin density distribution of azanion and protonated/deprotonated radical anion species were assessed by correlating the observed IR changes to the predicted vibrational frequencies and based on calculated structural parameters. The obtained information may enhance the understanding of the possible routes for metabolizing and interaction of flutamide with biomolecules relevant to its therapeutic action.

Списание [J Molec Structure 1271 \(2023\) 133927 \(1\)](#)

**68. Заглавие** Study on the Neuroprotective, Radical-Scavenging and MAO-B Inhibiting Properties of New Benzimidazole Arylhydrazones as Potential Multi-Target Drugs for the Treatment of Parkinson's Disease

**Автори** N. Anastassova, D. Aluani, N. Hristova-Avakumova, V. Tzankova, M. Kondeva-Burdina, M. Rangelov, N. Todorova, D. Yancheva

**Резюме** Oxidative stress is a key contributing factor in the complex degenerating cascade in Parkinson's disease. The inhibition of MAO-B affords higher dopamine bioavailability and stops ROS formation. The incorporation of hydroxy and methoxy groups in the arylhydrazone moiety of a new series of 1,3-disubstituted benzimidazole-2-thiones could increase the neuroprotective activity. In vitro safety evaluation on SH-SY5Y cells and rat brain synaptosomes showed a strong safety profile. Antioxidant and neuroprotective effects were evaluated in H<sub>2</sub>O<sub>2</sub>-induced oxidative stress on SH-SY5Y cells and in a model of 6-OHDA-induced neurotoxicity in rat brain synaptosomes, where the dihydroxy compounds **3h** and **3i** demonstrated the most robust neuroprotective and antioxidant activity, more pronounced than the reference melatonin and rasagiline. Statistically significant MAO-B inhibitory effects were exerted by some of the compounds where again the catecholic compound **3h** was the most potent inhibitor similar to selegiline and rasagiline. The most potent antioxidant effect in the ferrous iron induced lipid peroxidation assay was observed for the three catechols—**3h** and **3j**, **3q**. The catecholic compound **3h** showed scavenging capability against superoxide radicals and antioxidant effect in the iron/deoxyribose system. The study outlines a perspective multifunctional compound with the best safety profile, neuroprotective, antioxidant and MAO-B inhibiting properties.

Списание [Antioxidants 11 \(2022\) 884 \(1\)](#)

**69. Заглавие** Synthesis of new triazole and thiadiazole derivatives of the N,N'-disubstituted benzimidazole-2-thione and evaluation of their antitumor potential

**Автори** N. Anastassova, I. Georgieva, V. Milanova, R. Tzoneva, K. Radev, D. Yancheva, A. Mavrova

**Резюме** In the present study series of triazole-, thiadiazole- and thiosemicarbazone-benzimidazole hybrid compounds were synthesized as potential anti-cancer agents. In order to determine their antitumor potential and cytotoxic effect (via MTT assay) lung adenocarcinoma (A549) and breast cancer (MDA-MB-231) cell lines were examined. For detection of apoptosis induced by drug treatment, DAPI staining was performed in order to observe the apoptotic alterations in cell nuclei. It was found that the thiadiazole derivative 12 leads to the occurrence

of micronuclei, suggesting genotoxic effect. Furthermore, a wound healing assay was performed in order to test whether any changes in cell motility occurred upon treatment with the newly synthesized hybrids, since both cell lines are examples of highly invasive tumours. The cell motility of MDA-MB-231 was impeded mostly by compound 12 (15 % of wound closure) and in A549 compound 9 reduced cell motility by 46 % compared to the control. The obtained results suggest that compound 12 possesses a promising anticancer effect.

**Списание** [J Chem Technol Metallurgy 57\(4\) \(2022\) 709](#)

**70. Заглавие** Model for photodegradation with a modified rate constant part 1: use of anodically-prepared thin ZnO films for methyl orange photodegradation

**Автори** E. Lilov, V. Lilova, S. Nedev, S. Kozhukharov, C. Girginov, D. Yancheva

**Резюме** Four sets of samples of anodically prepared ZnO thin films were tested as potential photocatalysts for degradation of methyl orange (MO). The results show that the best properties belong to the samples prepared by anodization in oxalic acid and subsequently annealed 3 hours at 341°C. The dependences of the rate of the reaction on the time of use of the photocatalyst, the temperature of the decomposition reaction, the pH of the solution and the illumination were investigated too. The activation energies of the reactions were derived from the dependence of the rate of the reaction on the temperature. The properties of the acquired ZnO anodic films, as well as their compositions and structures were investigated by various analytical techniques, as follows: Attenuated Total Reflection Fourier Transformation Infrared Spectroscopy (ATR-FTIR), X-ray Diffractometry (XRD), Atomic Force Microscopy (AFM), Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES), Scanning Electron Microscopy (SEM) and UV-VIS Spectrophotometry

**Списание** [J Chem Technol Metallurgy 57\(5\) \(2022\) 919](#)

**71. Заглавие** Silver nanoparticles synthesis and their effect on the SOPC lipid structure

**Автори** Z. Slavkova, J. Genova, H. Chamati, V. Boev, D. Yancheva

**Резюме** We focus our attention on the influence of hydrophobic silver nanoparticles (Ag NPs) on the 1-Stearoyl-2-oleoylsn-glycero-3-phosphocholine (SOPC) model system. Results obtained by differential scanning calorimetry (DSC) and infrared (IR) spectroscopy were compared to their counterpart for lipid systems with incorporated hydrophobic gold nanoparticles (AuNPs) and pure SOPC lipid in a water environment. The results show a strong effect of hindering the gel-to-liquid crystalline phase transition for both types of noble metal hydrophobic NPs. The effect of the phase transitions shift to the lower temperatures is more pronounced for the silver particles for the concentrations studied. According to the IR spectral

analyses, no negative effect is observed of the NPs on the lipid hydration for the concentration studied, and the plasmon effect of the Ag NPs appears to be more pronounced.

Списание [J Physics: Conf Series 2240 \(2022\) 012019](#)

## *МОДУЛ 2*

### **1. Заглавие** Archaeometric Study of Belt Fittings to Late Antiquity in Bulgaria

**Автори** L. Traykova, B. Zlateva, D. Lesigyarski, V. Mihaylova, L. Vagalinski, I. Kuleff

**Резюме** The current investigation is a continuation of the project about the chemical composition of belt fittings dated from the end of the 3 rd c. to the first half of the 7 th c. AD in Bulgaria and covers archaeological finds from different geographical regions. In this study, we analyzed 169 samples (buckles, plate of buckles, strap-end and tongues of buckles) by portable XRF and ICP-AES was used for a selection. The main advantage of p-XRF spectrometry is the possibility to analyze objects on the spot, almost without causing any damage, which is very important for finds with very high historical and museum exposition value. The results show that only 11 buckles were made from silver, and the rest belt fittings were made from various kinds of copper alloys, such as bronze, brass, semi-red brass, gunmetal, etc.

Списание [Archaeologia Bulgarica XXVI \(2\) \(2022\) 39](#)

### **2. Заглавие** [Храмът на Кибела в Дионисополис. Интердисциплинарно изследване върху полихромията на архитектурните елементи и скулптурите \(книга\).](#)

**Автори** Р. Манова, Б. Рангелов, Г. Авдеев

**Издателство** „Българи“, София, 2022

### **3. Заглавие** Георги - един неизвестен аристократ от Калиакра / Georgi: An Unknown Aristocrat from Kaliakra (книга/book)

**Автори** Б. Петрунова, Г. Чокоев, Р. Пеевски / B. Petrunova, G. Chokoev, R. Peevski

**Издателство** „Уникарт“, София, 2022 / „Unicart“, Sofia, 2022