Šljukić, B., Milikić, J., Santos, D.M.F., Sequeira, C.A.C., Macciò, D., Saccone, A.
Electrocatalytic performance of Pt-Dy alloys for direct borohydride fuel cells
(2014) Journal of Power Sources, 272, pp. 335-343.

https://doi.org/10.1016/j.jpowsour.2014.08.080

ABSTRACT: The electrochemical oxidation of sodium borohydride (NaBH4) is systematically studied on platinum-dysprosium (Pt-Dy) alloys in alkaline media with respect to application in direct borohydride fuel cells (DBFCs). Using several different techniques, namely cyclic voltammetry, chronoamperometry and chronopotentiometry, reaction parameters are evaluated for NaBH4electrooxidation in 2 M NaOH supporting electrolyte. The values obtained for the number of electrons exchanged are comparable for the two alloys and close to 2.5. Dependence of Pt-Dy alloys activity for NaBH4oxidation on the electrolyte composition and temperature is also investigated. Test fuel cell is assembled using Pt-Dy alloy as anode, reaching peak power density of 298 mW cm-2at current density of 595 mA cm-2and cell potential of 0.5 V at 25 °C. Pt-Dy alloys exhibit comparable behavior with pure Pt electrode at room temperature, while at higher temperature they exhibit improved Coulombic efficiency, with the advantage of significantly lower price. © 2014 Elsevier B.V. All rights reserved.

Pejin, B., Mojovic, M., Savic, A.G.
Novel and highly potent antitumour natural products from cnidarians of marine origin
(2014) Natural Product Research, 28 (24), pp. 2237-2244.

https://doi.org/10.1080/14786419.2014.934241

ABSTRACT: This article covers the 2003-2012 literature published for marine natural products from the phylum Cnidaria. The focus is on new and highly potent antitumour substances, together with details related to the organism sourced. It describes 12 promising bioactives isolated from 7 species. © 2014 Taylor & Francis.

Bacher, F., Dömötör, O., Kaltenbrunner, M., Mojović, M., Popović-Bijelić, A., Gräslund, A., Ozarowski, A., Filipovic, L., Radulović, S., Enyedy, E.A., Arion, V.B.
Effects of terminal dimethylation and metal coordination of proline-2-formylpyridine thiosemicarbazone hybrids on lipophilicity, antiproliferative activity, and hR2 RNR inhibition
(2014) Inorganic Chemistry, 53 (23), pp. 12595-12609.

https://doi.org/10.1021/ic502239u

ABSTRACT: The nickel(II), copper(II), and zinc(II) complexes of the proline-thiosemicarbazone hybrids 3-methyl-(S)-pyrrolidine-2-carboxylate-2-formylpyridine thiosemicarbazone (l-Pro-FTSC or (S)-H2L1) and 3-methyl-(R)-pyrrolidine-2-carboxylate-2-formylpyridine thiosemicarbazone (d-Pro-FTSC or (R)-H2L1), as well as 3-methyl-(S)-pyrrolidine-2-carboxylate-2-formylpyridine 4,4-dimethyl-thiosemicarbazone (dm-l-Pro-FTSC or (S)-H2L2), namely, [Ni(l-Pro-FTSC-2H)]2 (1), [Ni(d-Pro-FTSC-2H)]2 (2), [Ni(dm-l-Pro-FTSC-2H)]2 (3), [Cu(dm-l-Pro-FTSC-2H)] (6), [Zn(l-Pro-FTSC-2H)] (7), and [Zn(d-Pro-

FTSC-2H)] (8), in addition to two previously reported, [Cu(l-Pro-FTSC-2H)] (4), [Cu(d-Pro-FTSC-2H)] (5), were synthesized and characterized by elemental analysis, one- and two-dimensional 1H and 13C NMR spectroscopy, circular dichroism, UV-vis, and electrospray ionization mass spectrometry. Compounds 1-3, 6, and 7 were also studied by single-crystal X-ray diffraction. Magnetic properties and solid-state high-field electron paramagnetic resonance spectra of 2 over the range of 50-420 GHz were investigated. The complex formation processes of l-Pro-FTSC with nickel(II) and zinc(II) were studied in aqueous solution due to the excellent water solubility of the complexes via pH potentiometry, UV-vis, and 1H NMR spectroscopy. The results of the antiproliferative activity in vitro showed that dimethylation improves the cytotoxicity and hR2 RNR inhibition. Therefore, introduction of more lipophilic groups into thiosemicarbazone-proline backbone becomes an option for the synthesis of more efficient cytotoxic agents of this family of compounds. © 2014 American Chemical Society.

Vujković, M., Paunković, B.S., Simatović, I.S., Mitrić, M., Sequeira, C.A.C., Mentus, S.
Versatile insertion capability of Na1.2V3O8 nanobelts in aqueous electrolyte solutions
(2014) Electrochimica Acta, 147, pp. 167-175.

ABSTRACT: Single phase nanobelt-like Na1.2V3O8 was synthesized by precipitation from aqueous solution of V2O5, H2O2 and NaOH, and subsequent annealing at 400 oC. The product was characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. As measured by both galvanostatic charging/discharging and cyclic voltammetry methods, in air-equilibrated aqueous electrolyte solutions containing nitrates of lithium, sodium and magnesium, this compound displayed fast intercalation/deintercalation reactions. The galvanostatic charging and discharging curves observed at rates ranging 500-7000 mA g-1, did not display clear plateaus characteristic of phase changes. The discharging capacities were found to range 101-35, 55-17 and 67-22 mAh g-1 for Li, Na and Mg intercalation, respectively. By cyclic voltammetry, for the sweep rates increasing in the range 5-400 mV s-1 (roughly 9-700 C), the capacity was found to decrease within the limits 63-35 mAh g-1 for Li+ intercalation, and 40 -11 mAh g-1 for Na+ and Mg2+ intercalation, respectively. By analyzing the dependence log (current) versus log (sweep rate), the interval of potentials corresponding to preferably diffusion control of intercalation/deintercalation processes was determined. © 2014 Elsevier Ltd. All rights reserved.

Samolov, A., Dragović, S., Daković, M., Bačić, G.
Analysis of 7Be behaviour in the air by using a multilayer perceptron neural network
(2014) Journal of Environmental Radioactivity, 137, pp. 198-203.

ABSTRACT: A multilayer perceptron artificial neural network (ANN) model for the prediction of the 7Be behaviour in the air as the function of meteorological parameters was developed. The model was optimized and tested using 7Be activity concentrations obtained by standard gamma-ray

spectrometric analysis of air samples collected in Belgrade (Serbia) during 2009-2011 and meteorological data for the same period. Good correlation (r = 0.91) between experimental values of 7Be activity concentrations and those predicted by ANN was obtained. The good performance of the model in prediction of 7Be activity concentrations could provide basis for construction of models which would forecast behaviour of other airborne radionuclides. © 2014 Elsevier Ltd.

Mudrinić, T., Mojović, Z., Milutinović-Nikolić, A., Banković, P., Dojčinović, B., Vukelić, N., Jovanović, D.
Beneficial effect of Ni in pillared bentonite based electrodes on the electrochemical oxidation of phenol
(2014) Electrochimica Acta, 144, pp. 92-99.

https://doi.org/10.1016/j.electacta.2014.07.115

ABSTRACT: The influence of Ni on the electrochemical performance of Fe containing bentonite-based electrode materials was investigated in the electrochemical oxidation of phenol in acidic solution. Clay originated from Mečji Do, Serbia, was submitted to pillaring. Mixed pillaring solutions containing Al3+and Fe3+or Al3+, Fe3+and Ni2+were used for this purpose. The XRD, chemical and FTIR analysis and nitrogen physisorption at -196 °C were used for sample characterization. The electrochemical behavior of the pillared clay-based electrodes was tested by cyclic voltammetry. The results confirmed that the pillaring was successful. The presence of Ni in the electrode material enhanced the electrode stability. It is possible that the presence of Ni restricted the electrode fouling caused by the formation of polymeric products during the electrooxidation of phenol. © 2014 Elsevier Ltd. All rights reserved.

Nikolić, I., Karanović, L., Častvan, I.J., Radmilović, V., Mentus, S., Radmilović, V.
Improved compressive strength of alkali activated slag upon heating
(2014) Materials Letters, 133, pp. 251-254.

https://doi.org/10.1016/j.matlet.2014.07.021

ABSTRACT: This paper presents a study on thermal stability of alkali activated slag (AAS) prepared from electric arc furnace slag (EAFS) using a mixture of alkaline sodium hydroxide and sodium silicate solutions. The samples were investigated by means of XRD, SEM, TG/DTA and porosity analysis. Compressive strengths of AAS samples before and after exposure to elevated temperatures ranging from 600 °C to 1000°C were determined. The significant microstructural modifications highlighted by changes in porosity due to the sintering process are responsible for the strengthening of AAS sample after heating at 600,800 and 1000°C. Moreover, in AAS sample after heating to and above 600 °C wüstite transforms to spinel. © 2014 Elsevier B.V.

Tomić, N.M., Dohčevic-Mitrovic, Z.D., Paunović, N.M., Mijin, D.Z., Radić, N.D., Grbić, B.V., Aškrabić, S.M., Babić, B.M., Bajuk-Bogdanović, D.V.
Nanocrystalline CeO2-δ as effective adsorbent of azo dyes
(2014) Langmuir, 30 (39), pp. 11582-11590.

ABSTRACT: Ultrafine CeO2-δ nanopowder, prepared by a simple and cost-effective self-propagating room temperature synthesis method (SPRT), showed high adsorption capability for removal of different azo dyes. Batch type of adsorption experiments with fixed initial pH value were conducted for the removal of Reactive Orange 16 (RO16), Methyl Orange (MO), and Mordant Blue 9 (MB9). The equilibrium adsorption data were evaluated using Freundlich and Langmuir isotherm models. The Langmuir model slightly better describes isotherm data for RO16 and MO, whereas the Freundlich model was found to best fit the isotherm data for MB9 over the whole concentration range. The maximum adsorption capacities, determined from isotherm data for MO, MB9, and RO16 were 113, 101, and 91 mg g-1 respectively. The adsorption process follows the pseudo-second-order kinetic model indicating the coexistence of chemisorption and physisorption. The mechanism of azo dye adsorption is also discussed. © 2014 American Chemical Society.

Ležaić, A.J., Pašti, I., Vukomanović, M., Ciric-Marjanovic, G.
Polyaniline tannate - Synthesis, characterization and electrochemical assessment of superoxide anion radical scavenging activity
(2014) Electrochimica Acta, 142, pp. 92-100.

ABSTRACT: Polyaniline tannate (PANI-TA) solid microspheres were synthesized by the external-template-free oxidative polymerization of aniline with ammonium peroxydisulfate (APS) in aqueous solution of tannic acid (TA). Syntheses were performed using fixed mole ratio [TA]/[aniline] and varying [APS]/[aniline] mole ratios and polymerization times. PANI-TA materials were characterized by scanning and transmission electron microscopies, FTIR and Raman spectroscopies, elemental microanalysis and conductivity measurements, and their structure and properties were compared. The ability of PANI-TA microspheres to act as antioxidants was investigated by cyclic voltammetry using the electrocatalytical reduction of O2 to the superoxide anion radical (•O2 -) and analyzing the evolution of the electrochemical response upon successive addition of PANI-TA as a radical scavenger. All synthesized materials showed very good •O 2 - scavenging activity. It was shown that the scavenging activity of PANI-TA can be tuned by the conditions of its synthesis, thus leading to the material showing higher antioxidant activity than pure TA. Observed differences in radical scavenging activities of PANI-TA materials were discussed. © 2014 Published by Elsevier Ltd.

Janković, B., Stopić, S., Friedrich, B.
Kinetic–Statistical Approach in a Detailed Study of the Mechanism of Thermal Decomposition of Zinc-Iron-Intermetallic Phase
(2014) Transactions of the Indian Institute of Metals, 67 (5), pp. 629-650.

ABSTRACT: Kinetic–statistical approach was applied to investigate the mechanism of thermal decomposition of Zinc–Iron-intermetallic phase, as by product from neutral leach residues. In present paper, in order to characterize the tested material, the following experimental techniques

were used: Rietveld analysis, scanning electron micrograph and tube furnace sample heating procedure. Based on dependence of Avrami constant in function of effective activation energy, it was found that at $T > 950\ ^{\circ}C$, the process of crystal growth takes place in autocatalytic stage, under the conditions, where rate of nucleation rapidly increases. It was established that high nucleation rate can be attributed to formation of both Zn and Fe rich regions which provide a high number of heterogeneous nucleation sites. It has been proposed that emergence of line defects under ZnO branched crystals can serve as pin-points for secondary nucleation to occur. It was confirmed that increase in temperature in Zn vapor did not result in a decrease of existing in Zn constitutional vacancies. © 2014, Indian Institute of Metals.

Stanisavljev, D.R., Velikić, Z., Veselinović, D.S., Jacić, N.V., Milenković, M.C.
Bray-Liebhafsky oscillatory reaction in the radiofrequency electromagnetic field
(2014) Chemical Physics, 441, pp. 1-4.

https://doi.org/10.1016/j.chemphys.2014.06.017

ABSTRACT: Oscillatory Bray-Liebhafsky (BL) reaction is capacitively coupled with the electromagnetic radiation in the frequency range 60-110 MHz. Because of the specific reaction dynamics characterized by several characteristic parameters (induction period, period between chemical oscillations and their amplitude) it served as a good model system for the investigation of the effects of radiofrequent (RF) radiation. RF power of up to 0.2 W did not produce observable changes of the BL reaction parameters in the limit of the experiment reproductivity. Results indicate that, under the given experimental conditions, both dissipative and reactive properties of the solution are not considerably coupled with the RF electrical field. © 2014 Elsevier B.V. All rights reserved.

Zdravković, J., Poleti, D., Rogan, J., Minić, D.M.
Bis(2,2'-bipyridine)-bis(μ3-phthalato)-dicopper(II) tetrahydrate as molecular sieve with zero-dimensional structure
(2014) Polyhedron, 80, pp. 256-264.

https://doi.org/10.1016/j.poly.2014.05.026

ABSTRACT: Crystal structure of the title compound: [Cu2(bipy) 2(pht)2]·4H2O (bipy = 2,2'-bipyridine, pht = dianion of phthalic acid), CuBP·4H 2O, consists of dinuclear entities, which are further connected by π-π stacking interactions between bipy ligands. In this way small channels (micropores) oriented parallel to the [0 0 1] direction and containing loosely hydrogen bonded water molecules are formed. The structural changes during dehydration-rehydration have been thoroughly investigated using TG/DSC analysis, FT-IR spectroscopy, X-ray powder diffraction, optical and scanning electron microscopy, and sorption experiments. In addition, dehydration process was analyzed from the aspect of kinetics. A complete reversibility of the dehydration-rehydration CuBP·4H2O(s) CuBP(s) + 4H 2O(g) process was confirmed by all means. Therefore, CuBP·4H2O can be classified as molecular sieve with quite unexpected zero-dimensional structure. © 2014 Elsevier Ltd. All rights reserved.

Shafaat, H.S., Griese, J.J., Pantazis, D.A., Roos, K., Andersson, C.S., Popović-Bijelić, A., Gräslund, A., Siegbahn, P.E.M., Neese, F., Lubitz, W., Högbom, M., Cox, N.
Electronic structural flexibility of heterobimetallic Mn/Fe cofactors: R2lox and R2c proteins
(2014) Journal of the American Chemical Society, 136 (38), pp. 13399-13409.

https://doi.org/10.1021/ja507435t

ABSTRACT: The electronic structure of the Mn/Fe cofactor identified in a new class of oxidases (R2lox) described by Andersson and Hö gbom [Proc. Natl. Acad. Sci. U.S.A. 2009, 106, 5633] is reported. The R2lox protein is homologous to the small subunit of class Ic ribonucleotide reductase (R2c) but has a completely different in vivo function. Using multifrequency EPR and related pulse techniques, it is shown that the cofactor of R2lox represents an antiferromagnetically coupled MnIII/FeIII dimer linked by a μ-hydroxo/bis-μ-carboxylato bridging network. The MnIII ion is coordinated by a single water ligand. The R2lox cofactor is photoactive, converting into a second form (R2lox Photo) upon visible illumination at cryogenic temperatures (77 K) that completely decays upon warming. This second, unstable form of the cofactor more closely resembles the MnIII/FeIII cofactor seen in R2c. It is shown that the two forms of the R2lox cofactor differ primarily in terms of the local site geometry and electronic state of the MnIII ion, as best evidenced by a reorientation of its unique 55Mn hyperfine axis. Analysis of the metal hyperfine tensors in combination with density functional theory (DFT) calculations suggests that this change is triggered by deprotonation of the μ-hydroxo bridge. These results have important consequences for the mixed-metal R2c cofactor and the divergent chemistry R2lox and R2c perform. © 2014 American Chemical Society.

Begović, N., Blagojević, V.A., Ostojić, S.B., Micić, D.M., Filipović, N., Andjelković, K., Minić, D.M.
Thermally induced structural transformations of a series of palladium(II) complexes with N-heteroaromatic bidentate hydrazone ligands
(2014) Thermochimica Acta, 592, pp. 23-30.

https://doi.org/10.1016/j.tca.2014.08.005

ABSTRACT: Thermal stability of a series of palladium(II) complexes with N-heteroaromatic bidentate hydrazone ligands was investigated using a combination of experimental measurements and DFT calculations. All complexes exhibit a reversible second-order transition around 333 K, which can be attributed to structural reorganization of the ligand molecules. Thermal degradation begins in 570-610 K temperature region, with an endothermic peak, followed by exothermic peaks in DSC. TG measurements show a well-defined mass loss corresponding to the initial degradation, while subsequent processes are poorly separated. DFT calculations suggest that the initial degradation step occurs with release of Cl, which then reacts with remaining part of the complex molecule in an exothermic process. This leads to decomposition of the ligand molecule into four fragments corresponding to ethyl chloride, carbon dioxide, methyl amine, and the fragment with the aromatic group.

Mass spectrum suggests that creation of these fragments most likely corresponds to the initial degradation, after which some of these coordinate to Pd center, whose coordination sphere is left incomplete by release of Cl. TG measurement to 1123 K indicates that the final degradation product at this temperature is palladium. © 2014 Elsevier B.V.

Pejin, B., Nakarada, D., Novakovic, M., Tesevic, V., Savic, A., Radotic, K., Mojovic, M.
Antioxidant volatiles of the freshwater bryozoan Hyalinella punctata
(2014) Natural Product Research, 28 (18), pp. 1471-1475.

ABSTRACT: Two volatile samples of the bryozoan Hyalinella punctata (seasonally collected from the same locality) were isolated (hydrodistillation, Clevenger apparatus), identified (GC and GC-MS) and screened in vitro (EPR) for anti-hydroxyl radical activity. The main components of sample 1 (2-ethyl-1-hexanol 37.00%, dodecanol 21.40% and hexanal 8.40%) and sample 2 (2-ethyl-1-hexanol 30.50%, 7-tridecanol 24.60% and 1-hexadecanol 11.80%) were relatively similar. However, more components were present in the sample 2 (17 and 25, respectively). EPR measurements indicated significant anti-hydroxyl radical activity of the both samples (75.00 ^ 6.00% and 87.00 ± 8.00%, respectively) whereas the generation of other types of free radicals in reaction with hydroxyl radicals was not observed. According to the best of our knowledge, this is the first report of 31 organic compounds from the phylum Bryozoa. Alcohols, aldehydes, ketones, esters and ethers of lower molecular mass appear to be characteristic for the volatiles of these organisms commonly known as moss animals. © 2014 Taylor & Francis.

Sarvan, M., Radić-Perić, J., Kasalica, B., Belča, I., Stojadinović, S., Perić, M.
Investigation of long-duration plasma electrolytic oxidation of aluminum by means of optical spectroscopy
(2014) Surface and Coatings Technology, 254, pp. 270-276.

ABSTRACT: The process of plasma electrolytic oxidation of aluminum was investigated by means of optical spectroscopy at a very long time interval. The change of morphology of obtained oxide coatings in the course of time was studied. Several hundreds of low-resolution emission optical spectra in the wavelength region between 250. nm and 850. nm, and higher-resolution spectra in the region from 230. nm to 290. nm were taken at the time interval up to 300. min from the beginning of the anodization. The spectra consisted of spectral lines and bands originating both from the anode material (Al, i.e. AlO) and the electrolyte (water solution of the boric acid and sodium tetraborate). Three pairs of spectral lines of aluminum were used to estimate the plasma temperature. It was found to be about 8000. K at the beginning of the process and as low as 3000-4000. K after roughly 1. h. The composition of the plasma containing aluminum, oxygen, hydrogen, and sodium was calculated in the temperature range up to 11,000. K under assumption of local thermal equilibrium, in order to explain the appearance of the observed spectral features. © 2014 Elsevier B.V.

Pavićević, A.A., Popović-Bijelić, A.D., Mojović, M.D., Šušnjar, S.V., Bačić, G.G.
Binding of doxyl stearic spin labels to human serum albumin: An EPR study
(2014) Journal of Physical Chemistry B, 118 (37), pp. 10898-10905.

https://doi.org/10.1021/jp5068928

ABSTRACT: The binding of spin-labeled fatty acids (SLFAs) to the human serum albumin (HSA) examined by electron paramagnetic resonance (EPR) spectroscopy was studied to evaluate the potential of the HSA/SLFA/EPR technique as a biomarking tool for cancer. A comparative study was performed on two spin labels with nitroxide groups attached at opposite ends of the fatty acid (FA) chain, 5-doxyl stearic (5-DS) and 16-doxyl stearic (16-DS) acid. The effects of incubation time, different [SLFA]/[HSA] molar ratios, ethanol, and temperature showed that the position of the nitroxide group produces certain differences in binding between the two SLFAs. Spectra for different [SLFA]/[HSA] molar ratios were decomposed into two spectral components, which correspond to the weakly and strongly bound SLFAs. The reduction of SLFA with ascorbate showed the existence of a two component process, fast and slow, confirming the decomposition results. Warfarin has no effect on the binding of the two SLFAs, whereas ibuprofen significantly decreases the binding of 5-DS and has no effect on 16-DS. Together, the results of this study indicate that both SLFAs, 5-DS and 16-DS, should be used for the study of HSA conformational changes in blood induced by various medical conditions. © 2014 American Chemical Society.

Jovanović, S.P., Marković, Z.M., Kleut, D.N., Dramićanin, M.D., Holclajtner-Antunović, I.D., Milosavljević, M.S., La Parola, V., Syrgiannis, Z., Todorović Marković, B.M.
Structural analysis of single wall carbon nanotubes exposed to oxidation and reduction conditions in the course of gamma irradiation
(2014) Journal of Physical Chemistry C, 118 (29), pp. 16147-16155.

https://doi.org/10.1021/jp502685n

ABSTRACT: Single wall carbon nanotubes (SWCNTs) were exposed to gamma irradiation in oxidative (H2O, NH4OH) and reductive (H2O and NH4OH both mixed with isopropyl alcohol) media. The structure has been investigated with microscopic (atomic force and transmission electron microscopy), spectroscopic (Raman, X-ray photoelectron, and FTIR spectroscopy) techniques, and by thermogravimetric analysis. Reductive media offer the possibility for green chemistry reduction of SWCNTs: after gamma irradiation, SWCNTs lose C-O bonds. Furthermore, irradiation in these media increases the fraction of sp2 hybridized carbon atoms in structure of SWCNTs and prevents their amorphization. The presence of isopropyl alcohol in reductive media contributed to the preservation of structure's unity. On the other hand, the most effective procedure is the one that occurs in oxidative media and yields in debundled, cut, and annihilated carbon nanotubes. The smaller diameter and the metallic ones are the most affected. © 2014 American Chemical Society.

Nikolic, V.M., Perovic, I.M., Gavrilov, N.M., Pašti, I.A., Saponjic, A.B., Vulic, P.J., Karic, S.D., Babic, B.M., Marceta Kaninski, M.P.
On the tungsten carbide synthesis for PEM fuel cell application – Problems, challenges and advantages
(2014) International Journal of Hydrogen Energy, 39 (21), pp. 11175-11185.

https://doi.org/10.1016/j.ijhydene.2014.05.078

ABSTRACT: Fuel cell application of tungsten carbide is revisited starting with four different tungsten carbide precursors used for high temperature synthesis. It was shown that the final products greatly depend on the nature of the precursor. Using tungsten peroxide/2-propanol derived precursor almost pure WC was obtained which was subjected to further electrochemical investigation. It was shown that it is necessary to decorate WC with Pt nanoparticles in order to obtain satisfactory fuel cell performance, but catalytic activity of Pt/WC anode catalyst is not expected to overcome the activity of Pt/C. It is argued that new synthetic routes for the preparation of WC should be directed towards obtaining highly dispersed WC, that is, WC with high external surface area available for Pt deposition, rather than high specific surface area WC with large contribution of micropores having no importance when it comes to the use of WC as a catalyst support. The true benefit of the use of WC as catalyst support is found in increased CO tolerance/CO oxidation activity of WC-supported Pt catalysts. Qualitative mechanistic view on increased CO oxidation activity of Pt/WC is offered. © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Kisić, D., Nenadović, M., Štrbac, S., Adnadjević, B., Rakočević, Z.
Effect of UV/ozone treatment on the nanoscale surface properties of gold implanted polyethylene
(2014) Applied Surface Science, 307, pp. 311-318.

https://doi.org/10.1016/j.apsusc.2014.04.032

ABSTRACT: The effect of ultraviolet (UV) ozone treatment on the surface properties of gold implanted high density polyethylene (HDPE) was investigated at a nanoscale using Atomic Force Microscopy (AFM). HDPE samples were modified by the implantation of gold ions at a dose of 5×10^{15} ions/cm^2, using energies of 50, 100, 150, and 200 keV, and subsequently treated with UV/ozone. AFM surface topography images revealed that after UV/ozone treatment, the surface roughness of all Au/HDPE samples increased, while Power Spectral Density function increased only for samples implanted using higher energies, with a maximum for 150 keV. The chemical surface composition was homogenous in all cases, which was evidenced by the appearance of single peaks in the histograms obtained from the phase AFM images. For UV/ozone treated samples, the shift of the peaks positions in the histograms to the higher values of the phase lag with respect to untreated ones indicated the decrease of surface hardness. Besides, a significant change of fractal dimension of surface grains is observed after UV/ozone treatment. © 2014 Elsevier B.V. All rights reserved.

Ciric-Marjanovic, G., Mentus, S., Pašti, I., Gavrilov, N., Krstić, J., Travas-Sejdic, J., Strover, L.T., Kopecká, J., Moravková, Z., Trchová, M., Stejskal, J.

Synthesis, characterization, and electrochemistry of nanotubular polypyrrole and polypyrrole-derived carbon nanotubes
(2014) Journal of Physical Chemistry C, 118 (27), pp. 14770-14784.

ABSTRACT: Polypyrrole nanotubes (PPy-NTs) were prepared by the oxidation of pyrrole with iron(III) chloride in the presence of a structure-guiding agent, methyl orange. Upon carbonization of the salt form of PPy-NTs, the conducting nitrogen-containing nanotubular carbonaceous material (C-PPy-NT) was obtained. The morphology, structure, and physicochemical properties of PPy-NTs in salt and base form as well as C-PPy-NTs were investigated by transmission electron microscopy, Fourier transform infrared and Raman spectroscopies, conductivity measurements, elemental microanalysis, inductively coupled plasma optical emission spectroscopy, X-ray photoelectron spectroscopy, and nitrogen physisorption. Results of the material characterization were linked to their electrochemical behavior. Specific capacitance of around 120 F'g-1 at low potential sweep rate of 5 mVs-1 was observed for original PPy-NTs. However, when the potential sweep rate was increased to 100 mVs -1, PPy-NT salt retained the value of specific capacitance, while the capacitance of PPy-NT base decreased by 70%. Upon carbonization of PPy-NT salt, the specific capacitance was doubled and capacitance fade measured in the interval 5-100 mVs-1 was determined to be around 45%. It is proposed that the absolute value of specific capacitance is determined by specific surface area and surface functional groups, while the capacitance fade is determined by the conductivity of the electrode material. In this manner, a linear relationship between the percent of capacitance fade and the logarithm of the conductivity was revealed. C-PPy-NTs were also tested as an electrocatalyst for the oxygen reduction reaction (ORR) in alkaline media. High ORR activity was observed, characterized by the onset potential of -0.1 V versus saturated calomel electrode and the apparent number of electrons consumed per oxygen molecule higher than 3. Appreciable ORR activity can be linked with a high fraction of mesopores and the presence of surface functional groups, especially pyridinic and pyrrolic nitrogens, and also with a high degree of structural disorder. © 2014 American Chemical Society.

Rakić, A.A., Trifunović, S., Ćirić-Marjanovic, G.
Dopant-free interfacial oxidative polymerization of aniline
(2014) Synthetic Metals, 192, pp. 56-65.

ABSTRACT: Polyaniline (PANI) was synthesized by the oxidation of aniline with ammonium peroxydisulfate (APS) as an oxidant in an immiscible organic/aqueous biphasic system, without added acid. An organic phase contained aniline dissolved in chloroform, while the oxidant was dissolved in water. The produced PANIs have conductivities in the range 0.008-0.1 S cm-1. Their nanogranular morphology was confirmed by scanning electron microscopy (SEM). Molecular structure of synthesized PANIs was investigated by FTIR, Raman, and UV-Vis spectroscopies, and elemental analysis. The influence of mechanical stirring and reaction time on the yield of polymerization, structure, and properties of synthesized PANIs was studied. The differences in the molecular structure, morphology, and conductivity between PANI prepared

by dopant-free interfacial polymerization and PANI prepared by corresponding polymerization in monophasic aqueous system are discussed. The results are also compared with the literature data on the interfacial polymerizations of aniline with APS in the presence of acids. © 2014 Elsevier B.V.

Pašti, I.A., Gavrilov, N.M., Mentus, S.V.
DFT study of chlorine adsorption on bimetallic surfaces - Case study of Pd3M and Pt3M alloy surfaces
(2014) Electrochimica Acta, 130, pp. 453-463.

ABSTRACT: Chlorine adsorption on Pd3M and Pt3M alloy surfaces (M = Fe, Co, Ni, Rh, Pd, Pt) with ideal bulk surface composition and Pt and Pd-skin type surfaces was analyzed by means of spin-polarized periodic Density Functional Theory calculations. The Pd-based surfaces tended to adsorb chlorine more strongly than the Pt-based surfaces. On bimetallic surfaces, Cl preferred to adsorb on the high-coordination sites. The ratio of surface stabilities, that is the preference of non-segregated surfaces or the skin-type ones, can be inverted under chlorine chemisorption conditions. The relative surface stability was linked to catalytic activity of Pt3Ni surfaces towards the oxygen reduction reaction in chloride-containing solutions. The charge transfer from metallic substrate to the Cl adatom was found to become more pronounced when the position of the solute M in the Periodic Table of Elements moved upward and left. However, the degree of bond ionicity did not exceed 20% in any case. In order to contribute to the comprehension of the adsorption trends, the Cl adsorption energy was correlated to the charge transfer parameters and to the electronic structure of the investigated bimetallic surfaces. © 2014 Elsevier Ltd.

Amić, A., Marković, Z., Dimitrić Marković, J.M., Stepanić, V., Lučić, B., Amić, D.
Towards an improved prediction of the free radical scavenging potency of flavonoids: The significance of double PCET mechanisms
(2014) Food Chemistry, 152, pp. 578-585.

ABSTRACT: The 1H+/1e- and 2H+/2e- proton-coupled electron transfer (PCET) processes of free radical scavenging by flavonoids were theoretically studied for aqueous and lipid environments using the PM6 and PM7 methods. The results reported here indicate that the significant contribution of the second PCET mechanism, resulting in the formation of a quinone/quinone methide, effectively discriminates the active from inactive flavonoids. The predictive potency of descriptors related to the energetics of second PCET mechanisms (the second O-H bond dissociation enthalpy (BDE2) related to hydrogen atom transfer (HAT) mechanism, and the second electron transfer enthalpy (ETE2) related to sequential proton loss electron transfer (SPLET) mechanism) are superior to the currently used indices, which are related to the first 1H+/1e- processes, and could serve as primary descriptors in development of the QSAR (quantitative structure-activity relationships) of flavonoids. © 2013 Elsevier Ltd. All rights reserved.

Vasić, M.M., Minić, D.M., Blagojević, V.A., Minic, D.M.

Kinetics and mechanism of thermally induced crystallization of amorphous Fe73.5Cu1Nb3Si15.5B7 alloy
(2014) Thermochimica Acta, 584, pp. 1-7.

ABSTRACT: Thermal stability of amorphous Fe73.5Cu1Nb 3Si15.5B7 alloy and its crystallization kinetics and mechanism have been investigated. The alloy is stable up to 748 K, after which it undergoes multi-step crystallization with formation of α-Fe(Si)/Fe3Si, Fe2B, Fe16Nb 6Si7, and Fe2Si crystalline phases. The crystallization occurs in two distinct and well separated complex processes, each corresponding to formation of two phases. Activation energy for the formation of the latter two phases is significantly higher, due to their formation out of the previously formed iron-silicon crystalline phase. By comparison of Avrami exponents of experimental system and a hypothetical system where no impingement occurs, the influence of impingement on reaction mechanism was successfully isolated. While the reaction mechanism was suggested as volume diffusion controlled growth of α-Fe(Si) and Fe2B phases, and interface-controlled growth of Fe16Nb6Si7 and Fe2Si phases, impingement plays an increasingly significant role as the crystallization progresses. The determined value of kinetic triplet was used to calculate the alloy lifetime, showing its resistance against crystallization. © 2014 Elsevier B.V.

Blagojević, V.A., Vasić, M., David, B., Minić, D.M., Minić, D.M., Pizúrová, N., Žák, T.
Microstructure and functional properties of Fe73.5Cu 1Nb3Si15.5B7 amorphous alloy
(2014) Materials Chemistry and Physics, 145 (1-2), pp. 12-17.

ABSTRACT: Fe73.5Cu1Nb3Si15.5B7 amorphous alloy undergoes a series of thermally induced structural transformations in temperature region between 25 and 800 C, including structural relaxation, two Curie temperatures and crystallization. The changes in microstructure caused by these transformations are characterized in detail using XRD, TEM, Mössbauer spectroscopy and EDX elemental analysis. Mössbauer spectroscopy, in particular, reveals that there is a very small degree of crystallinity in the as-prepared alloy, which is lost during structural relaxation after annealing at temperatures below 400 C. In addition, it suggests that crystallization of the alloy is much more complex process than suggested by XRD data, with several metastable intermediate phases serving as precursors to crystallization of stable crystalline phases. Magnetic, electrical and mechanical properties of the alloys are heavily influenced by the observed structural changes, most notably during crystallization of the alloy, where formation of crystalline phases and creation of new types of interfaces are the main factor to determine the performance of the alloy. © 2014 Elsevier B.V.

Stojmenović, M., Momčilović, M., Gavrilov, N., Pašti, I.A., Mentus, S., Jokić, B., Babić, B.
Incorporation of Pt, Ru and Pt-Ru nanoparticles into ordered mesoporous carbons for efficient oxygen reduction reaction in alkaline media
(2014) Electrochimica Acta, 153, pp. 130-139.

ABSTRACT: Ordered mesoporous carbon, volume-doped up to 3 w.% with Pt, Ru and Pt-Ru nanoparticles was synthesized by evaporation-induced self-assembly method, under acidic conditions. The content of incorporated metal was determined by EDX analysis. The X-ray diffractometry confirmed the existence of highly dispersed metallic phases in doped samples. Specific surface area was determined by N2-physisorption measurements to range between 452 and 545 m2 g-1. Raman spectroscopy of investigated materials indicated highly disordered carbon structure with crystallite sizes around 1.4 nm. In a form of thin-layer electrode on glassy carbon support, in 0.1 M KOH solution, the prepared materials displayed high activity toward oxygen reduction reaction (ORR) in alkaline media, with onset potentials more positive than -0.10 V vs. SCE. The kinetics of O2 reduction was found to be affected by both the specific surface area and the concentration of metal dopants. The ethanol tolerance of (Pt, Ru)-doped OMCs was found to be higher than that of common Pt/C ORR catalysts. Presented study provides a new route for the synthesis of active and selective ORR catalysts in alkaline media, being competitive with, or superior to, the existing ones in terms of performance and price. © 2014 Published by Elsevier Ltd.

Janković, B., Stopić, S., Güven, A., Friedrich, B.
Kinetic modeling of thermal decomposition of zinc ferrite from neutral leach residues based on stochastic geometric model
(2014) Journal of Magnetism and Magnetic Materials, 358-359, pp. 105-118.

ABSTRACT: The stochastic geometric model was applied to kinetic modeling the complex process of thermal decomposition of zinc ferrite from neutral leach residues, at different operating temperatures (600 C, 750 C, 950 C and 1150 C). Based on functional dependence of Avrami×s constant (n) in a function of the effective activation energy (Ea), it was found that at T>950 C, the crystallization process takes place in autocatalytic stage, under the conditions where the rate of nucleation rapidly increases. It was established that the high nucleation rate can be attributed to formation of both Zn and Fe rich regions which provide a high number of heterogeneous nucleation sites. Based on the obtained final shape of the particles, it was found a strong presence of zinc, iron (present only in the form of Fe3O4 (magnetite)), magnesium (in the form of Mg2Si2O 6), and also lead oxides. Thermodynamic analysis showed that the decomposition depends on the introduction of heat, and exerts a positive value of the Gibbs free energy of activation. Such a feature was expected since the ferrite system has been submitted to a forced decomposition and volatilization reactions. © 2014 Elsevier B.V.

Momčilović, M., Stojmenović, M., Gavrilov, N., Pašti, I., Mentus, S., Babić, B.
Complex electrochemical investigation of ordered mesoporous carbon synthesized by soft-templating method: Charge storage and electrocatalytical or Pt-electrocatalyst supporting behavior
(2014) Electrochimica Acta, 125, pp. 606-614.

ABSTRACT: Ordered mesoporous carbon (OMC) was synthesized by an evaporation induced self-assembly method, under acidic conditions, with resorcinol as the carbon precursor and Pluronic F127 triblock copolymer (EO106PO 70EO106) as a structure directing agent. The obtained OMC product was characterized by N2 sorptometry, X-ray diffractometry and Raman spectroscopy. The mean pore radius of 2 nm and specific surface area of 712 m2 g-1 were found. The OMC sample was subjected to a complex electrochemical testing in order to check for its applicability in various energy conversion processes. For pure OMC, the charge storage properties and kinetics of oxygen reduction reaction (ORR) in alkaline solution were measured. The OMC sample delivered specific capacitance of 232 F g-1 at 5 mV s-1 with 83.6% capacitance retained at 100 mV s-1. Effective ORR electrocatalysis by OMC in alkaline media was evidenced, with onset potential amounting to -0.10 V vs. saturated calomel electrode. A part of the OMC sample was used as a support of Pt nanoparticles, and examined as electrocatalyst for hydrogen evolution reaction (HOR) and ORR in acidic media. Reversible HOR kinetics was observed, while ORR performances were found to be competitive to the ones on other carbon-supported Pt electrocatalysts reported so far. A superb electrochemical behavior was correlated to physico-chemical properties of OMC. Described OMC stands out as a highly versatile material, which can be used to replace carbon materials developed for specific purposes, allowing rationalization of carbon-based technologies aimed for energy conversion purposes. © 2014 Elsevier Ltd.

Janković, B.Ž.
The pyrolysis behavior of lignins: Contemporary kinetics overview
(2014) Lignin: Structural Analysis, Applications in Biomaterials and Ecological Significance, pp. 329-374.

ABSTRACT: Lignin, a valuable resource for chemicals and energy, is a main component of wood, together with cellulose and hemicelluloses. It is the second large source of organic raw material, constituting about 4-35wt% of most biomass, 16-25wt% of hardwoods and 23- 35 wt% of softwoods. As most abundant natural aromatic polymer, lignin has a highly branched three-dimensional phenolic structure involving three main phenylpropane structural units (p-hydroxyphenyl, guaiacyl and syringyl units). Due to the very large generated quantities, lignin is increasingly considered as a potential source of chemicals, and studies on its thermal degradation receive much interest. Thermal degradation of lignin has mainly been investigated for three different purposes: (a) pyrolytic method is appropriate for investigating the structure of lignin due to rapid analysis using small amounts of samples, (b) reaction process of thermal degradation is necessarily required in order to produce carbon from lignin or wood charcoal, and (c) characterization is necessary in order to utilize decomposed materials as source of chemicals. Among various techniques in order to fulfill the above purposes, pyrolysis at isothermal condition, thermogravimetry (TG), simultaneous measurements of TG/Fourier transform infrared spectrometry (TG/FTIR), and TG/mass spectrometry (TG/MS) are used under both dynamic and static conditions. Knowledge of kinetics of thermal reactions is vital for predicting the pyrolysis behavior of lignin. Pyrolysis of lignin is highly complex and depends on several factors such as composition of lignin and processing conditions such as heating rate, reaction temperature and the carrier gas flow rate. Because of these factors, it is reasonable to optimise the lignin thermal

degradation process under appropriate process conditions. Once the satisfactory optimized process is established, the pyrolysis results will give reliable compositional information about differences among various types of lignins, originating from different biological sources. For this recognition, the great benefit for us may serve the kinetic parameters (such as activation energy and pre-exponential factor, together incorporated into a global mechanistic pattern), derived from lignin pyrolysis. Based on these facts, the research efforts are primarily focused on obtaining the kinetic parameters of lignin pyrolysis. However, in the literature, there is a great divergence about pyrolysis kinetics of lignins, which may be caused by the approaches to lignin extractions, the experimental techniques used to monitor the pyrolytic process, the accuracy of methods used to calculate the kinetic parameters, and also the way that was used in obtaining the mathematical functions of reaction mechanism for overall pyrolysis. This chapter provides an overview of the most important findings in area of lignin pyrolysis kinetics by discussing the impact of various factors, starting with effects of chemical and physical properties of different types of lignin, the experimental conditions (including the influence of heat and mass transfer processes), choices of kinetic methods and conditions for setting up the reaction models, on a comprehensive kinetic analysis. All phenomena will be discussed from the thermoanalytical (TA) measurements, in a dynamic (non-isothermal) mode.

Dimitrić Marković, J.M., Amić, D., Lučić, B., Marković, Z.S.
Oxidation of kaempferol and its iron(III) complex by DPPH radicals: Spectroscopic and theoretical study
(2014) Monatshefte fur Chemie, 145 (4), pp. 557-563.

https://doi.org/10.1007/s00706-013-1135-z

ABSTRACT: Kaempferol (3,5,7-trihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one), one of the most bioactive plant flavonoids, was quantitatively investigated for its ability to bind iron and scavenge DPPH radicals. The DPPH reduction test showed kaempferol and its iron complex to be less potent antioxidants towards DPPH radicals compared to structurally similar flavone molecules quercetin, baicalein, fisetin, morin, and their iron complexes. The equilibrium geometries of free and complexed kaempferol were optimized with the M05-2X functionals and 6-311G(d,p) basis set. Graphical abstract: [Figure not available: see fulltext.] © 2014 Springer-Verlag Wien.

Etinski, M., Rai-Constapel, V., Marian, C.M.
Time-dependent approach to spin-vibronic coupling: Implementation and assessment
(2014) Journal of Chemical Physics, 140 (11), art. no. 114104, .

https://doi.org/10.1063/1.4868484

ABSTRACT: In this work, we present the generalization of a time-dependent method for the calculation of intersystem crossing (ISC) rates in the Condon approximation. When ISC takes place between electronic states with the same orbital type, i.e., when the transition is forbidden according to the El-Sayed rules, it is necessary to go beyond the Condon approximation. Similar to the Herzberg-Teller

expansion of the vibronic interaction, the electronic spin-orbit matrix elements are assumed to depend linearly on the nuclear coordinates. The ISC rate is then a sum of three contributions: a direct, mixed direct-vibronic, and vibronic term. The method, presented in this work, is based on the generating function formalism and the multi-mode harmonic oscillator approximation. In addition to the zero-temperature case, we implemented formulae for finite-temperature conditions assuming a Boltzmann population of vibrational levels in the initial state. Tests have been carried out for a variety of molecules for which literature data were available. We computed vibronic one-photon spectra of free-base porphyrin and free-base chlorin and calculated ISC rates for xanthone, thioxanthone, thionine, as well as free-base porphyrin and found excellent agreement with previous results. Quantitative rates for triplet formation in rhodamine A have been determined theoretically for the first time. We find the $S1 \rightarrow T2$ channel to be the major source of triplet rhodamine formation in the gas phase. © 2014 AIP Publishing LLC.

Pejin, B., Savic, A., Sokovic, M., Glamoclija, J., Ciric, A., Nikolic, M., Radotic, K., Mojovic, M.
Further in vitro evaluation of antiradical and antimicrobial activities of phytol
(2014) Natural Product Research, 28 (6), pp. 372-376.

https://doi.org/10.1080/14786419.2013.869692

ABSTRACT: The antiradical activity of phytol was evaluated by electron paramagnetic resonance towards hydroxyl radical ($\cdot$OH), superoxide anion radical ($\cdot O_2$), methoxy radical ($\cdot CH_2OH$), carbon-dioxide anion radical ($\cdot O_2$), as well as towards nitric-oxide radical ($\cdot NO$) and 2,2-diphenyl-1-picrylhydrazyl ($\cdot DPPH$) radical. It reduced the production of all tested radicals showing more promising activity against $\cdot O_2$, $\cdot CH_2OH$ and $\cdot DPPH$ radicals (56%, 50% and 48%, respectively) in comparison with $\cdot NO$, $\cdot O_2$ and $\cdot OH$ radicals (38%, 23% and 15%, respectively). The antimicrobial activity of phytol was evaluated by the microdilution method against eight bacterial and eight fungal strains. To varying degrees, it was proven to be active against all tested bacteria and fungi (MIC 0.003-0.038 mg/mL and MBC 0.013-0.052 mg/mL, MIC 0.008-0.016 mg/mL and MFC 0.090-0.520 mg/mL, respectively). According to the obtained results, medical foods containing phytol may support development of new therapies for heart disease. © 2014 Taylor & Francis.

Janković, B., Čupić, Ž., Jovanović, D.
Non-isothermal reduction of silica-supported nickel catalyst precursors in hydrogen atmosphere: A kinetic study and statistical interpretation
(2014) Journal of the Iranian Chemical Society, 11 (6), pp. 1743-1758.

https://doi.org/10.1007/s13738-014-0447-1

ABSTRACT: A series of silica-supported nickel catalyst precursors was synthesized with different SiO_2/Ni mole ratios (0.20, 0.80 and 1.15). Non-isothermal reduction of Ni catalyst precursors was investigated by temperature-programmed reduction at four different heating rates (2, 5, 10 and 20 °C min-1), in a hydrogen atmosphere. Kinetic parameters (E_a, A) were determined using Friedman isoconversional method. It was found that for all mole ratios, apparent activation energy is practically

constant in conversion range of α = 30-70 %. In considered conversion range, the following values of apparent activation energy were found: E a = 129.5 kJ mol-1 (SiO2/Ni = 0.20), E a = 133.8 kJ mol-1 (SiO2/Ni = 0.80) and E a = 125.0 kJ mol-1 (SiO2/Ni = 1.15). Using two special functions (y(α) and z(α)), the kinetic model was determined. It was established that reduction of Ni catalyst precursors with different SiO2/Ni mole ratios is a complex process and can be described by two-parameter Šesták-Berggren (SB) autocatalytic model. Based on established values of SB parameters for each mole ratio, the possible mechanism was discussed. It was found that for all investigated ratios, the Weibull distribution function fits very well the experimental data, in the wide range of conversions (α = 5-95 %). Based on obtained values of Weibull shape parameter (θ), it was found that experimentally evaluated density distribution functions of the apparent activation energies can be approximated by the unbalanced peaked normal distribution. © 2014 Iranian Chemical Society.

Etinski, M., Tatchen, J., Marian, C.M.
Thermal and solvent effects on the triplet formation in cinnoline
(2014) Physical Chemistry Chemical Physics, 16 (10), pp. 4740-4751.

https://doi.org/10.1039/c3cp53247j

ABSTRACT: Cinnoline (1,2-diazanaphthalene) is of particular interest among the diazanaphthalenes. Its triplet quantum yield upon photoexcitation depends strongly on the temperature and the solvent environment. At the beginning of this study, the properties of the lowest triplet electronic state were not understood either. To elucidate the photophysics of cinnoline, we implemented algorithms based on the time-dependent approach for calculating intersystem crossing rates and one-photon spectra of thermally equilibrated vibronic levels. Our quantum chemical investigations reveal that the triplet formation in hydrocarbon solutions at low temperatures is an El-Sayed forbidden process. At higher temperatures and in hydroxylic solutions an additional El-Sayed allowed channel opens up, increasing the intersystem crossing rate substantially. Furthermore, we have solved the old puzzle concerning the character of the lowest triplet state of cinnoline. In the gas phase the electronic structure has mainly nπ* character with additional contributions from ππ* configurations since the nuclear arrangement in the pyridazine ring is not planar. In hydroxylic solvents, the electronic structure of the T1 state is altered. The simulation of the triplet emission shows that the experimentally observed phosphorescence of cinnoline in ethanol most certainly stems from the 3(ππ*) emission. © 2014 the Owner Societies.

Rakić, A.A., Vukomanović, M., Ciric-Marjanovic, G.
Formation of nanostructured polyaniline by dopant-free oxidation of aniline in a water/isopropanol mixture
(2014) Chemical Papers, 68 (3), pp. 372-383.

https://doi.org/10.2478/s11696-013-0453-2

ABSTRACT: Nanostructured polyaniline (PANI) was synthesised by the oxidation of aniline in a water/ isopropanol (propan-2-ol, IPA) (50 vol. %) mixture, without added acid, using ammonium peroxydisulfate (APS) as an oxidant. Influence of the IPA co-solvent and the reaction time on the molecular structure, morphology and properties of

synthesised PANI samples was studied by FTIR, Raman, and UV-VIS spectroscopies, scanning and transmission electron microscopies (SEM and TEM), and conductivity measurements. The course of the reaction was followed by monitoring changes in the temperature and acidity of the reaction medium. The results were compared with those obtained for PANI prepared in water without IPA under the same reaction conditions. The importance of the solvation effects, dielectric constant of the solvent, and the enthalpy of mixing of IPA with water on the course of the polymerisation reaction and on the properties of polymeric products in the water/IPA medium in comparison with those in water was pointed out. © 2013 Institute of Chemistry, Slovak Academy of Sciences.

Gordic, M., Bucevac, D., Ruzic, J., Gavrilovic, S., Hercigonja, R., Stankovic, M., Matovic, B.
Biomimetic synthesis and properties of cellular SiC
(2014) Ceramics International, 40 (2), pp. 3699-3705.

https://doi.org/10.1016/j.ceramint.2013.09.054

ABSTRACT: Biomorphous β-SiC ceramics were produced from several species of wood such as ash, wild cherry, black alder, Persian walnut, sessile oak and European hornbeam. The wood was pyrolysed, impregnated with tetraethyl orthosilicate (TEOS) sol in repeated cycles and thermally treated at 1800 C in vacuum. Four specimen groups included charcoal and three groups with 1, 3 and 5 cycles of impregnation were analyzed. Flexural and compressional strength of charcoal and woodlike SiC ceramics were measured using three-point and compression testing in different directions. Experimental results showed that mechanical properties of woodceramics were improved by repeating of impregnation cycles. Porosity measurement, dilatometric analysis, XRD and SEM analysis were used to study the macroscopical and microscopical properties of the resulting biomorphic SiC ceramics. © 2013 Elsevier Ltd and Techna Group S.r.l.

Micić, D., Šljukić, B., Zujovic, Z., Travas-Sejdic, J., Ćirić-Marjanović, G.
Electrocatalytic activity of carbonized nanostructured polyanilines for oxidation reactions: Sensing of nitrite ions and ascorbic acid
(2014) Electrochimica Acta, 120, pp. 147-158.

https://doi.org/10.1016/j.electacta.2013.12.069

ABSTRACT: A comparative study of the electrocatalytic activity of nitrogen-containing carbon nanomaterials, prepared by the carbonization of nanostructured polyaniline (PANI) salts, for the electrooxidation reactions is presented. Nanostructured PANI salts were synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in an aqueous solution in the presence of 5-sulfosalicylic acid (PANI-SSA), 3,5-dinitrosalicylic acid (PANI-DNSA) as well as without added acid (PANI), and subsequently carbonized to c-PANI-SSA, c-PANI-DNSA and c-PANI, respectively. Glassy carbon tip was modified with nanostructured c-PANIs and used for the investigation of sensing of nitrite and ascorbic acid in aqueous solutions as model analytes by linear sweep voltammetry. All three types of the investigated c-PANIs gave excellent response to the nitrite ions and ascorbic acid electrooxidation. The lowest peak potential for nitrite ion oxidation exhibited c-PANI (+0.87 V vs. SCE), and for ascorbic acid oxidation

both c-PANI and c-PANI-SSA (ca. + 0.13 V vs. SCE). Electrochemical data were correlated with structural and textural data obtained by Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, elemental and nitrogen sorption analysis. © 2013 Elsevier Ltd.

Milovanović, M.Z., Jerosimić, S.V.
Theoretical investigation of geometry and stability of small lithium-iodide LinI (n = 2-6) clusters
(2014) International Journal of Quantum Chemistry, 114 (3), pp. 192-208.

https://doi.org/10.1002/qua.24542

ABSTRACT: We present theoretical investigation of the structural characteristics and stabilities of neutral and positively charged LinI (n = 2-6) species. The structural isomers were found by using a randomized algorithm to search for minima structures, followed by B3LYP optimizations; the single-point RCCSD(T)/cc-pwCVTZ(-PP) calculations were performed in order to compute relative energies, binding energies per atom, adiabatic and vertical ionization energies, and dissociation energies. Stability was compared to the pure lithium clusters; there is a typical odd-even alternation; iodine doped clusters are more stable than pure lithium clusters. Lithium "cage" transfers its valence electron to the iodine atom to form neutral I - Lin+ and cationic I - Lin2+ clusters. An electron departures the lithium cage upon ionization. An important reason for the larger stability of closed-shell species is the existence of the HOMO 3c/2e natural bond orbitals. © 2013 Wiley Periodicals, Inc.

Popa, A., Sasca, V., Verdes, O., Barvinschi, P., Holclajtner-Antunović, I.
Acidic and neutral caesium salts of 12-molybdophosphoric acid supported on SBA-15 mesoporous silica. the influence of Cs concentration and surface coverage on textural and structural properties
(2014) Materials Research Bulletin, 50, pp. 312-322.

https://doi.org/10.1016/j.materresbull.2013.11.015

ABSTRACT: The Cs salts of molybdophosphoric acid $Cs_1H_2PMo_{12}O_{40}$ (Cs1PM) and $Cs_3PMo_{12}O_{40}$ (Cs3PM), were supported on SBA-15 in the concentration of 20, 30 and 40 wt.% loadings. Because Cs salts are insoluble, the SBA-15 supported Cs-acid salts were prepared by two-step sequential impregnation and in situ reaction on the support. The structure and texture of these CsPM/SBA-15 composites were studied by XRD, SEM-EDS, FT-IR and micro-Raman spectroscopy, UV-vis-DRS and N_2 adsorption. Thermal stability was investigated by thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The acidity of composites was studied by the adsorption of ammonia and its temperature programmed desorption - TPD using thermogravimetry. The evolved gases during the adsorption-desorption of ammonia on CsPM/SBA-15 composites were identified by online mass spectrometry coupled with thermal gravimetry technique. FT-IR and Raman studies demonstrated that CsPM maintained its Keggin structure after deposition on mesoporous SBA-15, regardless of the active phase concentration. For both $Cs_1H_2PMo_{12}O_{40}$ and $Cs_3PMo_{12}O_{40}$-SBA-15 composites could be observed an important increase of band gap energy in comparison with pure salts. The values of specific surface

area of pure CsPM were increased by deposition on mesoporous silica support. The immobilization of CsPM on mesoporous SBA-15 obviously increases the thermal stability and the total acidity of the strong acidic sites of the Keggin structures in comparison with their parent bulk Cs salts.

Tanasković, V., Pašti, I.A., Gavrilov, N., Mentus, S.V.
Dimethylsulfoxide as a modifier of platinum electrocatalytic activity toward oxygen reduction reaction in aqueous solutions: Combined theoretical and experimental study
(2014) Journal of Electroanalytical Chemistry, 714-715, pp. 11-18.

https://doi.org/10.1016/j.jelechem.2013.12.020

ABSTRACT: By both density functional theory calculations (DFT) and voltammetry on rotating polycrystalline platinum disc, dimethylsulfoxide (DMSO) was investigated as a modifier of platinum electrocatalytic activity toward oxygen reduction reaction in aqueous solutions. The DFT calculations evidenced that DMSO molecule interacts with Pt surface most strongly by the mediation of S atom in SO group, and the modification of the surface electronic structure of Pt is restricted to the Pt atom contacting directly with the S atom. The calculated adsorption energy on Pt surface (Pt(1 0 0)) amounted to -108 kJ mol -1. The voltammetry with polycrystalline Pt disk electrode in mixed H_2O-DMSO solutions supported by 0.1 mol dm-3 H_2SO_4 pointed out that DMSO adsorption suppressed oxide formation on Pt surface. In O_2-saturated solutions, in presence of 1 vol.% of DMSO, it was found that the rate of oxygen reduction reaction (ORR) was higher in comparison to the one measured in DMSO-free solution. It was also confirmed that adsorption of DMSO suppressed ethanol oxidation reaction in the entire potential window where ORR takes place. © 2013 Elsevier B.V. All rights reserved.

Čučulović, A.A., Pavlović, M.S., Savović, J.J., Veselinović, D.S.
Desorption of metals from cetraria islandica (L.) Ach. Lichen using solutions simulating acid rain
(2014) Archives of Biological Sciences, 66 (1), pp. 273-284.

https://doi.org/10.2298/ABS1401273C

ABSTRACT: Desorption of metals K, Al, Ca, Mg, Fe, Ba, Zn, Mn, Cu and Sr from Cetraria islandica (L.) with solutions whose composition was similar to that of acid rain, was investigated. Desorption of metals from the lichen was performed by five successive desorption processes. Solution mixtures containing H_2SO_4, HNO_3 and H_2SO_4-HNO_3 were used for desorption. Each solution had three different pH values: 4.61, 5.15 and 5.75, so that the desorptions were performed with nine different solutions successively five times, always using the same solution volume. The investigated metals can be divided into two groups. One group was comprised of K, Ca and Mg, which were desorbed in each of the five desorption processes at all pH values used. The second group included Al, Fe, Zn, Ba, Mn and Sr; these were not desorbed in each individual desorption and not at all pH values, whereas Cu was not desorbed at all under any circumstances. Using the logarithmic dependence of the metal content as a function of the desorption number, it was found that potassium builds two types of links and is connected with weaker links in lichen. Potassium is completely desorbed, 80% in

the first desorption, and then gradually in the following desorptions. Other metals are linked with one weaker link (desorption 1-38%) and with one very strong link (desorption below the metal detection limit).

Stevanović, S., Tripković, D., Tripković, V., Minić, D., Gavrilović, A., Tripković, A., Jovanović, V.M.
Insight into the effect of Sn on CO and formic acid oxidation at PtSn catalysts
(2014) Journal of Physical Chemistry C, 118 (1), pp. 278-289.

https://doi.org/10.1021/jp408207u

ABSTRACT: The role of Sn on the catalytic activity for CO and formic acid oxidation is studied by comparing the activities of differently treated PtSn/C and Pt/C catalysts. The catalysts are prepared by a microwave-assisted polyol synthesis method. As revealed by scanning tunneling and transmission electron microscopic (STM and TEM) characterization, the outcomes of the synthesis procedure for both Pt and PtSn are small particles, ~1.5 nm in diameter. Upon deposition on the carbon support, the particle size increases to ~2.5 nm due to sintering. X-ray diffraction (XRD) analysis shows that PtSn/C has a low alloying degree and is mainly composed of Pt and Pt_3Sn phases. The remaining Sn is present in the form of very small tin oxide particles. Different surfaces are obtained by double-layer, oxide, and CO annealing of the Pt/C and PtSn/C catalysts and by modifying the CO-annealed surfaces with irreversibly adsorbed tin, Snirr. The presence of Sn in any form (oxide, alloyed, or Snirr) on the surface shifts the onset potential for the CO oxidation negatively by more than 0.4 V in comparison to equivalently treated Pt/C catalysts. For the CO-annealed PtSn/C catalyst, a so-called skeleton structure, Sn is present only in the subsurface layers. The subsurface Sn has a mild effect on the CO activity, and hence the onset potential is only marginally shifted to cathodic potentials by ~50 mV compared to that on Pt/C. The formic acid oxidation is enhanced at any of the PtSn/C surfaces with Sn in the surface layer. The activity enhancement is explained by a reduced CO poisoning of the surface Pt sites. As a consequence, the current is not entering plateau as on the Pt/C catalysts. Furthermore, the skeleton PtSn/C is ~2 times more active than similarly treated Pt/C. The results have been substantiated and explained by comprehensive density functional theory (DFT) simulations. The DFT results indicate that the increased oxidation rates are not only due to surface Sn but also due to a weakened CO binding in the vicinity of the surface $SnOH_x$ moieties and SnO_2 particles. © 2013 American Chemical Society.

Stanisavljev, D.R., Ljubić, I.Z., Milenković, M.C.
Influence of chemically inert cations on the hydrogen-bond network in the bray-liebhafsky oscillatory reaction
(2014) Australian Journal of Chemistry, 67 (6), pp. 944-948.

https://doi.org/10.1071/CH14021

ABSTRACT: The influence of the chemically inert alkali metal cations on the Bray-Liebhafsky oscillatory reaction dynamics was investigated by the addition of the same amount of various sulfates to the reaction mixture. Beside the expected changes related to the altered acidity of

the sulfuric acid solution, subtle changes dependent on cation dimensions were noticed. Larger cations have more impact on the Bray-Liebhafsky reaction dynamics. Analysing the mean ionic activity of salts, it is suggested that the effects may be related to the altered extent of water hydrogen bonding and specific role of bulk water in the reaction mechanism. © CSIRO 2014.

Petković, M., Etinski, M.
Intramolecular OHO bonding in dibenzoylmethane: Symmetry and spectral manifestations
(2014) RSC Advances, 4 (73), pp. 38517-38526.

https://doi.org/10.1039/c4ra05586a

ABSTRACT: Although both experimentalists and theoreticians agree that dibenzoylmethane exists in the enol form, there are different opinions concerning symmetry of the OHO fragment. Consequently, assignment of its vibrational spectra has been incomplete. In this contribution we computed Gibbs free energies with the G4MP2 method. Multi-dimensional potential energy surfaces obtained at M06-2X/cc-pVTZ level enabled vibrational analysis and comparison with available experimental data. Our results revealed presence of two conformers in the gas phase at room temperature, the asymmetric structure (with O-H stretching frequency around 2400 cm-1 and very low infrared intensity), and the symmetric conformer (with O···H···O asymmetric stretching band located around 500 cm-1). Characterization of hydrogen bonds was performed with quantum theory of atoms in molecules (QTAIM), which showed that O-H···O group represents a typical hydrogen bond, whereas hydrogen bonds in the O···H···O fragment have substantial covalent character. © the Partner Organisations 2014.

Stojadinović, S., Vasilić, R., Perić, M.
Investigation of plasma electrolytic oxidation on valve metals by means of molecular spectroscopy-a review
(2014) RSC Advances, 4 (49), pp. 25759-25789.

https://doi.org/10.1039/c4ra03873h

ABSTRACT: A review of results of molecular spectroscopic investigations during plasma electrolytic oxidation of valve metals is presented. Particular attention is paid to three spectral systems, B1Σ+ → X 1Σ+ of MgO, and B2Σ+ → X2Σ+, and C2Π-X 2Σ+ of AlO. It was shown that a reliable assignment of the observed spectral features can only be carried out by critical comparison with the data obtained from high-resolution spectroscopy, and by using the results of quantum mechanical structure calculations. Assuming the existence of partial local thermal equilibrium, we used our spectroscopic results to determine the plasma temperature. Although limited in quality, the obtained spectra are very rich, they cover large wavelength regions, and are used to obtain information about physical and chemical processes that take place in the course of plasma electrolytic oxidation of light metals and their alloys. © the Partner Organisations 2014.

Nikolić, B., Milojević, N., Stanisavljev, D., Knežević-Vukčević, J.

Different effects of microwaves and conventional heating on bacteriophage and proliferation in E. coli
(2014) Archives of Biological Sciences, 66 (2), pp. 721-728.

https://doi.org/10.2298/ABS1402721N

ABSTRACT: The proliferation of bacteriophage λ in E. coli was used as a model to compare the effects of microwaves and conventional heating on cell metabolism. Irradiation was carried out in a single-mode focused reactor at 2.45 GHz, under an absorption rate of 0.8±0.1 W/g and at constant temperature (33°C or 37°C). The kinetic curve of phage release from cells irradiated at 37°C was decreased as compared to the control, but significantly increased at 33°C. This was attributed to local overheating of cells by microwaves. Based on the conventional heating experiments, performed at 33°C, 37°C, 41°C and 45°C, we estimated that microwave-induced overheating inside cells was between 4°C and 8°C. However, this should have a limited effect on virus proliferation at 33°C, contrary to the obtained results. The increased expression of heat shock proteins (HSP) was proposed to be responsible for the observed effect of microwaves on virus proliferation.

Popović, M.P., Vojnović, M.M., Aoneas, M.M., Ristić, M.M., Vićić, M.D., Poparić, G.B.
Ionization of N2 in radio-frequent electric field
(2014) Physics of Plasmas, 21 (6), art. no. 063504, .

https://doi.org/10.1063/1.4882438

ABSTRACT: Rate coefficients for the electron impact ionization of the N2 molecule are calculated in non-equilibrium conditions in the presence of time-dependent electric field. A Monte Carlo simulation has been developed in order to determine non-equilibrium electron energy distribution functions within one period of the radio-frequent (RF) electric field. By using these distribution functions, rate coefficients for ionization of the N2 molecule have been obtained time resolved within one period in the frequency range from 13.56 up to 500 MHz, at effective reduced electric field values up to 700 Td. This work presents an insight into the temporal characteristics of ionizing process and provides the ionization rate coefficients that can be of great use for correct implementation in modeling RF plasma discharges. A behavior of rate coefficients under the influence of magnitude and frequency of the fields was studied separately revealing some interesting features in time dependence. © 2014 AIP Publishing LLC.

Ostojić, B.D., Stanković, B., Dordević, D.S.
Theoretical study of the molecular properties of dimethylanthracenes as properties for the prediction of their biodegradation and mutagenicity
(2014) Chemosphere, 111, pp. 144-150.

https://doi.org/10.1016/j.chemosphere.2014.03.067

ABSTRACT: There is little information available on methyl derivatives of anthracene and their interaction with the enzymes of bacterial consortia that could be found in petroleum sludge. In this study a theoretical investigation of all dimethylanthracenes (DMA) isomers and their relation to biodegradation are presented. Equilibrium geometries,

ionization potentials (IP), electronic affinities (EA), dipole moments and electronic dipole polarizabilities of DMA isomers calculated by Density Functional Theory (DFT) methods are reported. The calculated IP and EA values vary little along the series of isomers. The polarizability values (α, δ α, and αyy) increase on passing from meso,meso- and α,meso- to β,β-DMA isomers. The computed polarizability values of DMAs can be used as predictors in determining differences in biodegradation rates of DMAs. The summation over Raman activity $\sum$. ARaman over 3N-6 vibrational modes is sensitive to the position of the methyl substituent. The $\sum$. ARaman values of 1-methylanthracene (MA), 2-MA, 2,9-DMA and 9,10-DMA are consistent with observed mutagenic activities in Salmonella Typhimurium strains TA98 and TA100. © 2014 Elsevier Ltd.

Ostojić, B.D., Stanković, B., Dordević, D.S.
The molecular properties of nitrobenzanthrone isomers and their mutagenic activities
(2014) Chemosphere, 104, pp. 228-236.

https://doi.org/10.1016/j.chemosphere.2013.11.057

ABSTRACT: The mutagenic activity of five mono-substituted nitrobenzanthrones (NBA) has been determined in the Ames assay (. Takamura-Enya et al., 2006). In the present study, a theoretical investigation of the electronic properties of all mono-substituted NBA isomers and their relation to mutagenic activity are presented. Equilibrium geometries, vertical ionization potentials (. VIP), vertical electron affinities (. VEA), relative energies, dipole moments and electronic dipole polarizabilities, and the IR and Raman spectra of NBA isomers calculated by Density Functional Theory (DFT) methods are presented. The position of the nitro group affects the spectral features of the IR and Raman spectra of the NBA isomers. The results show that a good linear relationship exists between the summation of Raman activities (. $\sum$ARaman) over all the 3N-6 vibrational modes and the mutagenic activity of the NBA isomers in Salmonella typhimurium strains. The spectroscopic results suggest that the unknown mutagenic activities of 4-NBA, 5-NBA, 6-NBA, 8-NBA and 10-NBA are predicted to follow the order 4-NBA. >. 10-NBA. >. 5-NBA. >. 8-NBA. >. 6-NBA. © 2013 Elsevier Ltd.

Kuzmanovic, M., Momcilovic, M., Ciganovic, J., Rankovic, D., Savovic, J., Milovanovic, D., Stoiljkovic, M., Pavlovic, M.S., Trtica, M.
Properties of plasma induced by pulsed CO2laser on a copper target under different ambient conditions
(2014) Physica Scripta, T162, art. no. 014011, .

https://doi.org/10.1088/0031-8949/2014/T162/014011

ABSTRACT: Optical emission spectroscopy was applied for investigation of copper plasma induced by a nanosecond transversely excited atmospheric CO2laser, operating at 10.6 µm. The effect of the background gas (air, Ar, He and N2) and pressure (1-25 mbar) on plasma formation was examined. The plasma shielding effect was more pronounced for background gases with lower ionization potential than for He. The increase of He pressure from 1 to 25 mbar resulted in fivefold increase of Cu atomic line intensity. © 2014 The Royal Swedish Academy of Sciences.

Kepić, D., Marković, Z., Jovanović, S., Holclajtner Antunović, I., Kleut, D., Todorović Marković, B.
Novel method for graphene functionalization
(2014) Physica Scripta, T162, art. no. 014024, .

ABSTRACT: In this paper we present a novel method to obtain a stable dispersion of graphene in water using carbon quantum dots as surface active agents. In this way it is possible to achieve graphene concentrations in dispersion up to 2.7 mg ml-1. Fourier transform infrared spectroscopy and UV-Vis measurements confirmed the presence of oxygen-containing functional groups in the graphene-carbon quantum dot (gCQD) structure, responsible for its good solubility in water. The stability of the gCQD dispersion is due to π-π interactions formed between graphene and graphene-like sites of carbon quantum dots. According to Raman spectroscopy, as well as transmission electron microscopy and atomic force microscopy analysis, graphene sheets consist of several layers. © 2014 The Royal Swedish Academy of Sciences.

Dragišic Maksimovic, J.J., Živanović, B.D., Maksimović, V.M., Mojović, M.D., Nikolic, M.T., Vučinić, T.B.
Filter strip as a method of choice for apoplastic fluid extraction from maize roots
(2014) Plant Science, 223, pp. 49-58.

ABSTRACT: Apoplastic fluid was extracted from maize (Zea mays L.) roots using two procedures: collection from the surface of intact plant roots by filter paper strips (AF) or vacuum infiltration and/or centrifugation from excised root segments (AWF). The content of cytoplasmic marker (glucose-6-phosphate, G-6-P) and antioxidative components (enzymes, organic acids, phenolics, sugars, ROS) were compared in the extracts. The results obtained demonstrate that AF was completely free of G-6-P, as opposed to AWF where the cytoplasmic constituent was detected even at mildest centrifugation (200. ×. g). Isoelectric focusing of POD and SOD shows the presence of cytoplasmic isoforms in AWF, and HPLC of sugars and phenolics a much more complex composition of AWF, due to cytoplasmic contamination. Organic acid composition differed in the two extracts, much higher concentrations of malic acid being registered in AF, while oxalic acid due to intracellular contamination being present only in AWF. EPR spectroscopy of DEPMPO spin trap in the extracts showed persistent generation of hydroxyl radical adduct in AF. The results obtained argue in favor of the filter strip method for the root apoplastic fluid extraction, avoiding the problems of cytoplasmic contamination and dilution and enabling concentration measurements in minute regions of the root. © 2014 Elsevier Ireland Ltd.

Okić-Djordjević, I., Trivanović, D., Jovanović, M., Ignjatović, M., Šećerov, B., Mojović, M., Bugarski, D., Bačić, G., Andjus, P.R.
Increased survival after irradiation followed by regeneration of bone marrow stromal cells with a novel thiolbased radioprotector
(2014) Croatian Medical Journal, 55 (1), pp. 45-49.

ABSTRACT: Aim: To investigate the survival of laboratory rats after irradiation and to study the cellularity of their bone marrow and the multipotential mesenchymal stem cells (BMMSCs) in groups treated with or without a new thiol-based radioprotector (GM2011) Methods Animals were irradiated by a Cobalt gamma source at 6.7 Gy. Treated animals were given i.p. GM2011 30 minutes before and 3 and 7 hours after irradiation. Controls consisted of sham irradiated animals without treatment and animals treated without irradiation. After 30 days post-irradiation, animals were sacrificed and bone marrow cells were prepared from isolated femurs. A colony forming unit-fibroblast (CFU-F) assay was performed to obtain the number of BM-MSCs. Results: In the treated group, 87% of animals survived, compared to only 30% in the non-treated irradiated group. Irradiation induced significant changes in the bone marrow of the treated rats (total bone marrow cellularity was reduced by ~60%- from 63 to 28 cells ×106/femur and the frequency of the CFU-F per femur by ~70%- from 357 to 97), however GL2011 almost completely prevented the suppressive effect observed on day 30 post-irradiation (71 cells × 106/femur and 230 CFU-F/femur). Conclusion: Although the irradiation dosage was relatively high, GL2011 acted as a very effective new radioprotector. The recovery of the BN-MSCs and their counts support the effectiveness of the studied radioprotector.

Damjanović, L., Bikić, V., Šarić, K., Erić, S., Holclajtner-Antunović, I.
Characterization of the early Byzantine pottery from Caričin Grad (South Serbia) in terms of composition and firing temperature
(2014) Journal of Archaeological Science, 46 (1), pp. 156-172.

ABSTRACT: Mineralogical and chemical composition as well as production methods of the pottery from Caričin Grad, a significant early Byzantine urban complex and production centre of the northern Illyricum region, were determined by multi-analytical investigations that comprised optical analysis and scanning electron microscopy with energy dispersive spectrometry (SEM-EDS), micro-Raman and Fourier transform infrared (FTIR) spectroscopy, and X-ray powder diffraction (XRPD) methods. The obtained data indicate that all investigated pottery samples were made of similar raw material that, most likely, originated from the local geological environment. Estimated firing temperatures for the cooking pots vary between 600°C and 900°C, while for the glazed table and storage vessels they are more uniform, about 900°C. The transparent high lead glaze was obtained by direct application of lead oxide to the ceramic surface. © 2014 Elsevier Ltd.

Kepić, D.P., Marković, Z.M., Jovanović, S.P., Peruško, D.B., Budimir, M.D., Holclajtner-Antunović, I.D., Pavlović, V.B., Todorović Marković, B.M.
Preparation of PEDOT:PSS thin films doped with graphene and graphene quantum dots
(2014) Synthetic Metals, 198, pp. 150-154.

ABSTRACT: Enhanced conductivity, transparency and stability are the most important factors to consider in order to prepare electrodes for optoelectronic devices. In this paper, we investigated the properties of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) films doped with graphene and graphene quantum dots. Samples were deposited by spin-coating onto glass substrates. Thin films were characterized by UV-vis and Raman spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and four-point probe measurements. It was found that both graphene and graphene quantum dots improve the conductivity of PEDOT:PSS films with only small decrease in transparency. AFM and SEM analysis showed homogenous distribution of spherical nanoparticles of graphene quantum dots and irregular shaped nanoparticles of graphene in PEDOT:PSS. © 2014 Elsevier B.V. All rights reserved.

Rajković, K., Bačić, G., Ristanović, D., Milošević, N.T.
Mathematical model of neuronal morphology: Prenatal development of the human dentate nucleus
(2014) BioMed Research International, 2014, art. no. 812351, .

https://doi.org/10.1155/2014/812351

ABSTRACT: The aim of the study was to quantify the morphological changes of the human dentate nucleus during prenatal development using mathematical models that take into account main morphometric parameters. The camera lucida drawings of Golgi impregnated neurons taken from human fetuses of gestational ages ranging from 14 to 41 weeks were analyzed. Four morphometric parameters, the size of the neuron, the dendritic complexity, maximum dendritic density, and the position of maximum density, were obtained using the modified Scholl method and fractal analysis. Their increase during the entire prenatal development can be adequately fitted with a simple exponential. The three parameters describing the evolution of branching complexity of the dendritic arbor positively correlated with the increase of the size of neurons, but with different rate constants, showing that the complex development of the dendritic arbor is complete during the prenatal period. The findings of the present study are in accordance with previous crude qualitative data on prenatal development of the human dentate nucleus, but provide much greater amount of fine details. The mathematical model developed here provides a sound foundation enabling further studies on natal development or analyzing neurological disorders during prenatal development. © 2014 Katarina Rajković et al.

Potkonjak, N.I., Nikolić, Z., Anić, S.R., Minić, D.M.
Electrochemical oscillations during copper electrodissolution/passivation in trifluoroacetic acid induced by current interrupt method
(2014) Corrosion Science, 83, pp. 355-358.

https://doi.org/10.1016/j.corsci.2014.02.034

ABSTRACT: Complex oscillatory behavior of electric current and electrode potential were observed during potentiodynamic anodic polarization of Cu in 1 M TFA, applying the current interrupt method for IR drop compensation. This oscillatory behavior was found to give an electrochemical response in the form of a polarization curve with continuous loop. The results presented show that the current interrupt

method is capable of eliminating the entire IR drop. Under such conditions, oscillations of the applied potential are in fact those of the double-layer potential. Theoretically predicted interplay between oscillatory behavior of the double-layer potential and the electric current is experimentally demonstrated. © 2014 Elsevier Ltd.

Milenković, M.C., Potkonjak, N.I.
The effect of hydroxycinnamic acids on oxy-radical generating iodide-hydrogen peroxide reaction
(2014) Bulletin of the Chemical Society of Japan, 87 (11), pp. 1255-1259.

https://doi.org/10.1246/bcsj.20140175

ABSTRACT: The influence of hydroxycinnamic acids (HCA) on the oxy-radical generated system, potassium iodide/hydrogen peroxide, was investigated through the enhancement of triiodide (I3 -) yield. Caffeic acid, chlorogenic acid, and p-coumaric acid were used as typical representatives of HCA. A linear correlation, with positive slopes, was found between absorption maximum of I3 - at 351 nm and HCA concentration in all cases. The magnitude of enhanced I3 - production was found to increase in the following order: p-coumaric acid < chlorogenic acid ≤ caffeic acid. A reaction mechanism, which includes negative influence of oxygen-centered free radicals on the I3 - yield, was proposed. The enhanced production of I3 - by HCA is attributed to their radical scavenging activity. Supported by literature data, results obtained in this study have showed the correlation between radical scavenging activities of HCA and their ability to enhanced I3 - generation. © 2014 The Chemical Society of Japan.

Pejin, B., Savic, A.G., Petkovic, M., Radotic, K., Mojovic, M.
In vitro anti-hydroxyl radical activity of the fructooligosaccharides 1-kestose and nystose using spectroscopic and computational approaches
(2014) International Journal of Food Science and Technology, 49 (6), pp. 1500-1505.

https://doi.org/10.1111/ijfs.12445

ABSTRACT: Fructooligosaccharides (FOS) are bioactive oligosaccharide fructans with beneficial health effects. Anti-hydroxyl radical activity is an important factor in the description of antioxidant capacity of any natural product. The aim of this study was to estimate in vitro anti-hydroxyl radical activity of the FOS 1-kestose and nystose by electron paramagnetic resonance spectroscopy (EPR) and fluorescence spectroscopy (FS) followed by a theoretical approach based on quantum chemistry calculations. A significant anti-hydroxyl radical potential of both compounds was observed (72% and 78% by EPR and 69% and 74% by FS, respectively), indicating the nystose to be a more active natural product. In addition, the computational results have confirmed that nystose follows the same pattern previously shown for 1-kestose, that is, that carbohydrates can react with hydroxyl radical. It is well known that FOS belong to cardioprotective nutraceuticals, so the study may be of some interest to research in heart disease. © 2013 Institute of Food Science and Technology.

Kleut, D.N., Marković, Z.M., Holclajtner Antunović, I.D., Dramićanin, M.D., Kepić, D.P., Todorović Marković, B.M.

Gamma ray-assisted irradiation of few-layer graphene films: A Raman spectroscopy study
(2014) Physica Scripta, T162, art. no. 014025, .

ABSTRACT: This paper represents results of a Raman spectroscopy study of gamma-irradiated few-layer graphene thin films at three different doses: 25, 50 and 110 kGy. Graphene thin films were deposited by the vacuum filtration method and then transferred onto glass substrate. Raman spectroscopy and atomic force microscopy analysis have shown that the average in-plane crystallite size Laof graphene thin films varies slightly when an irradiation dose is applied. Raman spectroscopy revealed that gamma irradiation of graphene thin films resulted in slight p-doping of the graphene thin film surface. It was found that during gamma irradiation at a dose of 110 kGy, the graphene sheets merged. As a result, the number of incorporated defects in the graphene structure was reduced (the ID/IGratio decreased with the increase in the applied dose). © 2014 The Royal Swedish Academy of Sciences.

Čučulović, A., Sabovljevič, M., Veselinovič, D.
The activity concentrations of 40K, 226Ra, 232Th, 238U and 7Be in moss from spas in eastern Serbia in the period 2000-2012
(2014) Archives of Biological Sciences, 66 (2), pp. 691-700.

ABSTRACT: In this work we present the activity concentrations of natural radionuclides 40K, 226Ra, 232Th, 238U and 7Be in mosses. One hundred and sixty-seven moss samples were collected between 2001 and 2012 from the territory of the Sokobanja, Banja Jošanica and Gamzigradska Banja spas. They were classified into 23 species. The activity concentrations (Bq/kg) in moss from Sokobanja spa were: 40K 25-427; 226Ra 0.3-36; 232Th 1.0-37; 238U 0.4-28 and 7Be 29-210; from Banja Jošanica spa they were: 40K 90-242; 226Ra 2.4-11.7; 232Th 2.0-12.7; 238U 1.6-11.3 and 7Be 142-212; Gamzigradska Banja spa: 40K 95-351; 226Ra 8.0-21; 232Th 5.1-19; 238U 6.7-18 and 7Be 20-144. The activity concentrations of dominant natural radionuclides (potassium, radium, thorium and uranium) in the moss samples were within the usual ranges for the territory of Serbia.

Vujković, M., Mentus, S.
Fast sodiation/desodiation reactions of electrochemically delithiated olivine LiFePO4 in aerated aqueous NaNO3 solution
(2014) Journal of Power Sources, 247, pp. 184-188.

ABSTRACT: By potentiodynamic polarization in saturated aqueous NaNO3 solution, the composite LiFePO4/C was transformed completely to NaFePO4/C composite. The voltammograms of sodiated olivine were successfully recorded at the rate for two order of magnitude higher than reported for the same material in organic electrolyte. A high storage capacity amounting to 118 mAh g-1 at a scan rate of 10 mV s-1 was measured. The diffusion coefficients have been calculated via cyclic voltammetry and faster diffusion of sodium in comparison to lithium was found. This finding was confirmed also with the impedance

Pavlovic, A.D., Ignjatovič, L.M., Popav, S.Z., Mladenović, A.R., Stanković, I.N.
Application of gas chromatography analysis to quality control of residual organic solvents in clopidogrel bisulfate
(2014) Journal of the Serbian Chemical Society, 79 (10), pp. 1279-1293.

https://doi.org/10.2298/JSC131120013P

ABSTRACT: A direct-injection, split-mode capillary gas chromatographic procedure with flame ionization detection was developed for the analysis of eight solvents used in the synthesis and purification of the anti-thrombotic drug clopidogrel bisulfate. The solvents analyzed were methanol, acetone, dichloromethane (DCM), 2-butanol, cyclohexane, toluene, acetic acid and N, N-dimethylformamide (DMF). In addition, because of dehydration of 2-butanol during the drying process, significant amounts of 2-butanol dehydration products (1-butene, cis- and trans-isomers of 2-butene, 2,2-oxybis[butane] and 1-(1- -methylpropoxy)butane) may be detected in clopidogrel bisulfate samples. The content of each of these volatile products can be evaluated using the same gaschromatographic method, with quantification based on the response factor established for the chromatographic peak of 2-butanol. Based on a large number of result sets, retrospectively, from many different batches analyzed, conclusions were made about process variations and reliability and a lack of consistency was identified in the quality of the active substance from a particular producer source. Multivariate analysis was used as the statistical technique to classify the samples. From the analyzed set of 11 solvents, 6 of them were preselected based upon their occurrence in the samples and both Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were performed.

Stojadinović, S., Radić-Perić, J., Vasilić, R., Perić, M.
Spectroscopic investigation of direct current (DC) plasma electrolytic oxidation of zirconium in citric acid
(2014) Applied Spectroscopy, 68 (1), pp. 101-112.

https://doi.org/10.1366/13-07198

ABSTRACT: Plasma electrolytic oxidation of zirconium in citric acid was investigated using optical spectroscopy. A rich emission spectrum consisting of about 360 zirconium and 170 oxygen atomic and ionic lines was identified in the spectral regions 313-320, 340-516, and 626-640 nm. It was shown that the remaining features observed in the spectrum could be ascribed to various molecular species, which involve zirconium, oxygen, hydrogen, and carbon. The temperature of the plasma core (T=7500 ± 1000 K) was determined using measured Zr line intensities, and the temperature of peripheral plasma zone (T = 2800 ± 500 K) was estimated from the intensity distribution within a part of an OH spectrum. The composition of the plasma containing zirconium, oxygen, and hydrogen, under assumption of local thermal equilibrium, was calculated in the temperature range up to 12 000 K and for pressure

of 105 and 10 7 Pa, in order to explain the appearance of the observed spectral features. © 2014 Society for Applied Spectroscopy.

Pejin, B., Savic, A., Kien-Thai, Y., Mojovic, M.
Further in vitro evaluation of antiradical activity of the moss Rhodobryum ontariense tea using EPR and fluorescence spectroscopy
(2014) Cryptogamie, Bryologie, 35 (2), pp. 173-179.

https://doi.org/10.7872/cryb.v35.iss2.2014.173

ABSTRACT: The moss Rhodobryum ontariense tea has been claimed by Traditional Chinese medicine for its beneficial effects in the treatment of wide range of cardiovascular diseases including hypertension. The antiradical activity of R. ontariense tea (i.e. its lyophilised water extract) was evaluated by electron paramagnetic resonance spectroscopy/against superoxide anion ($\cdot O_2-$), nitric-oxide ($\cdot NO$), 2,2-diphenyl-l- picrylhydrazyl ($\cdot DPPH$), carbon-dioxide anion ($\cdot CO_2$ -) and methoxy ($\cdot CH_2OH$) radicals/and fluorescence spectroscopy/against hydroxyl ($\cdot OH$) radicals/in in vitro conditions. It reduced the production of majority of radical species tested, but in a varying degree. The most activity was observed against $\cdot OH$, $\cdot DPPH$ and $\cdot CO_2-$ radicals (95 ± 10%, 78 ± 4% and 67 ± 5%, respectively). In addition, the extract was shown to be active against $\cdot CH_2OH$ and $\cdot NO$ radicals (55 ± 8% and 45 ± 8%, respectively). On the contrary, no any antiradical activity was observed against $\cdot O_2$ radicals. According to the experimental data obtained, R. ontariense tea can be considered as a promising resource of natural products with antiradical activity and may be of some interest to research in heart disease. © 2014 Adac. I ous droits réservé s.

Jankovic̈, B.
Kinetic modeling of native Cassava starch thermo-oxidative degradation using Weibull and Weibull-derived models
(2014) Biopolymers, 101 (1), pp. 41-57.

https://doi.org/10.1002/bip.22271

ABSTRACT: A new approach in kinetic modeling of thermo-oxidative degradation process of starch granules extracted from the Cassava roots was developed. Based on the thermoanalytical measurements, three reaction stages were detected. Using Weibull and Weibull-derived (inverse) models, it was found that the first two reaction stages could be described with the change of apparent activation energy (Ea) on conversion fraction ($\alpha(T)$) (using "Model- free" analysis). It was found that first reaction stage, which involves dehydration and evaporation of lower molecular mass fractions, can be described with an inverse Weibull model. This model with its distribution of Ea values and derived distribution parameters includes the occurrence of three-dimensional diffusion mechanism. The second reaction stage is very complex, and it was found to contain the system of simultaneous reactions (where depolymerization occurs), and can be described with standard Weibull model. Identified statistical model with its distribution of Ea values and derived distribution parameters includes the kinetic model that gives the variable reaction order values. Based on the established models, shelf-life studies for first two stages were carried out. Shelf-life testing has shown that optimal dehydration time is achieved by a programmed heating at medium heating rate, whereas

optimal time of degradation is achieved at highest heating rate. © 2013 Wiley Periodicals, Inc. Biopolymers 101: 41-57, 2014. Copyright © 2013 Wiley-Liss, Inc.

Janković, B.
The pyrolysis of coffee paper cup waste samples using non-isothermal thermo-analytical techniques. the use of combined kinetic and statistical analysis in the interpretation of mechanistic features of the process
(2014) Energy Conversion and Management, 85, pp. 33-49.

ABSTRACT: Pyrolysis process of coffee paper cup samples was investigated in a flow stream of nitrogen at different heating rates (10, 20, 30 and 40 °C min -1), using thermo-analytical techniques. It was found that second pyrolysis stage can be described by Šesták-Berggren (SB) autocatalytic model, with mechanism function f(α) = α 0.011(1 - α)1.459. Based on analysis of SB kinetic exponents (designated by M and N), it was found that second pyrolysis stage is mainly controlled by chemical process, involving reactions with reaction-order (n) higher than unity. Applying specific statistical analysis, in order to obtain precise distribution of reactivity, the discrete (binomial) distribution has shown that there are two important areas of current distribution for corresponding energy outcomes, within the apparent activation energy as random variable. The first "concentration" area of energy outcomes corresponds to start of chain end depolymerization reaction forming levoglucosan at high enough temperature region, while second "concentration" area of energy outcomes includes occurrence of macro-radicals in liquid phase propagate with radical addition on unsaturated C-C bonds, with cross-linking and formation of small chemical species. It was found that further elevating of temperature (above 340 °C), will leads to fact that rate of tar-forming reactions increases and formation of char decreases. © 2014 Elsevier Ltd. All rights reserved.

Marian, C.M., Etinski, M., Rai-Constapel, V.
Reverse intersystem crossing in rhodamines by near-infrared laser excitation
(2014) Journal of Physical Chemistry A, 118 (34), pp. 6985-6990.

ABSTRACT: The population of the long-lived first excited triplet state (T 1) of a fluorescence dye represents a major limitation in single-molecule spectroscopy. Reverse intersystem crossing (ReISC) is one of the processes that may prevent considerable loss of luminescence. In the present quantum chemical study we have analyzed rhodamine A in aqueous environment. The T2 ‡' S1 and T3 ‡' S2 ReISC channels are predicted to be viable. The rate constant computed for the former channel is ≈2 × 106 s-1. Hence, an excitation with suitable wavelength to one of the triplets should help repopulate the optically bright singlet state S1. © 2014 American Chemical Society.

Jakšić, O.M., Jakšić, Z.S., Čupić, Ž.D., Randjelović, D.V., Kolar-Anić, L.Z.

Fluctuations in transient response of adsorption-based plasmonic sensors
(2014) Sensors and Actuators, B: Chemical, 190, pp. 419-428.

ABSTRACT: The basic parameters of a sensor element defining its ultimate performance are sensitivity and intrinsic noise. In plasmonic gas sensors both are determined by refractive index changes due to adsorption and desorption (a-d) of target analyte particles to the sensor active area. In this paper we present a general model that can be simultaneously used to determine sensitivity and intrinsic noise of a plasmonic sensor both during transients and in steady-state and is valid for multi-analyte environments. The model utilizes the conventional probabilistic approach. It is derived without any assumptions about the stochastic nature of the fundamental (a-d) process. It reveals how all stochastic properties of the processes with (pseudo) first order kinetics with the initial number of particles equal to zero can be fully determined from the deterministic solution, without any previous stochastic analysis. Based on the proposed model it is possible to establish the optimum moment for readout when fluctuations are minimal. Transients last longer and fluctuations are lower at lower temperatures. The insight into the transient dynamics opens the possibility to use a single element sensor for multiple analyte sensing. Another result is that a-d noise is higher for smaller adsorption areas, which may be important for micro and nanosystems generally, since each of them has to be kept immersed in some kind of environment and thus be subject to contamination by adsorption that can significantly influence their behavior. Besides being applicable for plasmonic sensors of trace amounts of gases and other nanoplasmonic devices used in sensing, the model is applicable for other adsorption-based sensors, as well as for the investigations of stochastic phenomena in micro and nanostructures. © 2013 Elsevier B.V. All rights reserved.

Jakšić, O.M., Randjelović, D.V., Jakšić, Z.S., Čupić, T.D., Kolar-Anić, L.Z.
Plasmonic sensors in multi-analyte environment: Rate constants and transient analysis
(2014) Chemical Engineering Research and Design, 92 (1), pp. 91-101.

ABSTRACT: This paper investigates multicomponent gas adsorption at the active surface of plasmonic chemical sensors and shows that there are situations where transients in a single sensor element can be used for simultaneous detection of different gases in multicomponent mixtures. A general master equation set is provided, describing multicomponent adsorption. Analytical expressions for sorption rates are derived and high-accuracy simplified models are proposed. Expressions for adsorption rate constants and rates and for number of binding sites are proposed. The derived analytical model takes into account the adsorbate molecule size, distribution of binding sites as determined by the crystallographic structure of the sensor surface and multi-site adsorption. The model allows for the calculation and optimization of deterministic behavior of the system. It is shown that trace amounts of target gas species can be made detectable by adding controlled amounts

of known carrier gas. Besides being applicable in plasmonic sensor design and optimization, the obtained results may be of importance in situations where fast and low-cost detection of trace amounts of gases is needed, including natural gas leakage in residential heating, radon outgassing in dwellings, environmental protection, homeland defense and hazardous materials management, greenhouse footprint investigations, etc. © 2013 The Institution of Chemical Engineers.

Jakšić, O., Jokić, I., Jakšić, Z., Čupić, Ž., Kolar-Anić, L.
Adsorption-induced fluctuations and noise in plasmonic metamaterial devices
(2014) Physica Scripta, T162, art. no. 014047, .

https://doi.org/10.1088/0031-8949/2014/T162/014047

ABSTRACT: The investigation represented here is focused on fundamental intrinsic fluctuations caused by the adsorption and desorption (a-d) of surrounding particles on the active surface in plasmonic metamaterial devices. The variance and relative fluctuations in adsorption-desorption dynamics are studied based on two different kinetic models (pseudo-first order kinetics and second order kinetics). The limits of the applicability of the pseudo-first order model are determined, thus ensuring the use of the vast mathematical heritage developed for linear systems in calculation of a-d noise, while at the same time speeding up and simplifying calculations. An approach is proposed to assess adsorption in a metamaterial sensor using an effective parameter dependent on the properties of the metamaterial unit cell. © 2014 The Royal Swedish Academy of Sciences.

Janković, B., Marinović-Cincović, M., Dramićanin, M.D.
Study of non-isothermal crystallization of Eu3+ doped Zn 2SiO4 powders through the application of various macrokinetic models
(2014) Journal of Alloys and Compounds, 587, pp. 398-414.

https://doi.org/10.1016/j.jallcom.2013.10.240

ABSTRACT: Various macrokinetic models (Avrami, Evans, Tobin, Malkin, Dietz, Nakamura, and modified first-order models) were applied to describe non-isothermal crystallization kinetics of Eu3+ doped zinc silicate powders prepared via the sol-gel method. Analysis of the experimental data was carried out using a direct-fitting method such that the experimental data were fitted directly to each macrokinetic model using a non-linear multivariable regression computation procedure. Comparison of kinetic parameters obtained from the non-linear computation approach to those obtained from the traditional analytical procedure suggested that applicability and reliability of the direct-fitting method were satisfactory. Judging from the quality of the fit, only Nakamura's model properly describe the temperature dependence of the relative crystallinity, which resulted in the total rejection of the Tobin model in describing the crystallization. With detailed kinetic examination it was concluded that crystallization mechanism of α-willemite doped samples combusted in a microwave oven (MW) follows interface controlled growth with an increasing nucleation rate, attached with geometric process-rate function obeying the improved (corrected) Nakamura's model. It was found that the presence of non integer Avrami exponent values may indicate that crystallization occurs by more than one reaction mechanism, including the occurrence of

autocatalytic behavior of a given system. © 2013 Elsevier B.V. All rights reserved.

Bogdanović, U., Vodnik, V.V., Ahrenkiel, S.P., Stoiljković, M., Ćirić-Marjanović, G., Nedeljković, J.M.
Interfacial synthesis and characterization of gold/polyaniline nanocomposites
(2014) Synthetic Metals, 195, pp. 122-131.

https://doi.org/10.1016/j.synthmet.2014.05.018

ABSTRACT: Composites consisting of polyaniline (PANI) and gold nanoparticles (AuNPs) with an average size of 17 and 30 nm were synthesized by an interfacial method performed in an immiscible water/toluene biphasic system. The effect of embedded AuNPs on the morphology, structure and physicochemical properties of Au/PANI nanocomposites was investigated using scanning and transmission electron microscopies, UV-vis, FTIR, Raman and ICP-AES spectroscopies, X-ray diffraction, elemental analysis and conductivity measurements. Microscopy studies indicated nanofibrous morphology for pure PANI and Au/PANI nanocomposites, while FTIR and Raman spectroscopies were confirmed emeraldine salt form of PANI chains and the presence of phenazine units. Also, Raman spectroscopy measurements revealed an inherent structural inhomogeneity at the macromolecular level that exist in PANI chains in its pure form as well as in Au/PANI nanocomposites. In addition, the increase of the electrical conductivity observed in the nanocomposites was discussed. © 2014 Elsevier B.V.

Prekodravac, J.R., Jovanović, S.P., Holclajtner-Antunović, I.D., Peruško, D.B., Pavlović, V.B., Tošić, D.D., Todorović-Marković, B.M., Marković, Z.M.
Monolayer graphene films through nickel catalyzed transformation of fullerol and graphene quantum dots: A Raman spectroscopy study
(2014) Physica Scripta, T162, art. no. 014030, .

https://doi.org/10.1088/0031-8949/2014/T162/014030

ABSTRACT: In this paper we present synthesis of monolayer graphene islands. These films are deposited through nickel catalyzed transformation of fullerol and graphene quantum dots. Carbon doped nickel films are produced by autocatalytic chemical deposition. Upon rapid thermal annealing, graphene films are formed. Different characterization techniques are applied: Raman spectroscopy, scanning electron and atomic force microscopy. Raman spectroscopy analysis confirmed the formation of monolayer graphene films. Microscopy analysis revealed formation of monolayer islands. © 2014 The Royal Swedish Academy of Sciences.

Janković, B.Z., Janković, M.M.
Thermal characterization and isothermal kinetic analysis of commercial Creosote decomposition process
(2014) Journal of Thermal Analysis and Calorimetry, 115 (1), pp. 823-832.

https://doi.org/10.1007/s10973-013-3322-x

ABSTRACT: Isothermal decomposition process of commercial Creosote was analyzed by thermogravimetric technique in a nitrogen atmosphere, at four different operating temperatures (T = 230, 250, 270, and 290 C). It was found that the two-parameter autocatalytic Šesták-Berggren kinetic model best describes the investigated process. It was established that the applied logistic function can successfully perform a given kinetic predictions of investigated process, at all operating temperatures. The experimental density distribution function of the apparent activation energy values was evaluated. Based of the characteristic shape of distribution curve, it was concluded that the isothermal pyrolysis of commercial Creosote represent a complex process, which probably includes primary and secondary (autocatalytic) pyrolysis reactions, together with various decomposition reactions and radicals recombination pathways.

Radenković, M., Joksić, J., Miljanić, Š.
Synergy of chemical and isotopic signatures data for environmental fate studies
(2014) RAD Conference Proceedings, 2014-May, pp. 91-93.

ABSTRACT: Environmental fate study conducted for case of uranium contamination of the environment have been described and discussed in the paper as an example of combined application of radiochemical separation methods, spectrometric analytical techniques and elemental speciation procedures to obtain the most complete set of data for investigation of their correlations. As a result, isotopic and chemical composition, ratios of activities concentrations and indication of probable physicochemical forms and bonding with different substrates were obtained. Radiochemical ion-exchange separation procedures followed by alpha spectrometry analysis have shown the isotopic ratios of $238U$, $234U$ and $235U$ activity concentrations characteristic for depleted uranium. The isotopic signature of contaminant was determined on the basis of activity ratios $235U/238U$ and $234U/238U$. These isotopic ratios differ for natural and depleted uranium and their values in the soil samples or their components are corresponding to the amount of depleted uranium in total uranium content of the sample. In the fractions obtained after the soil samples underwent a series of successive solid/liquid chemical extractions simulating environmental conditions, depleted uranium contribution to the total uranium contents was calculated and analyzed together with data on chemical composition of fractions. Correlations derived from isotopic and stable elements concentrations determined in extraction phases after multistep sequential extraction indicated potential substrates and bonding potential. Although contamination was not widespread, on the basis of obtained data, environmental fate of contaminant in terms of geochemical fractionation and mobility may be indicated.

Volarevic, V., Paunovic, V., Markovic, Z., Simovic Markovic, B., Misirkic-Marjanovic, M., Todorovic-Markovic, B., Bojic, S., Vucicevic, L., Jovanovic, S., Arsenijevic, N., Holclajtner-Antunovic, I., Milosavljevic, M., Dramicanin, M., Kravic-Stevovic, T., Ciric, D., Lukic, M.L., Trajkovic, V.
Large graphene quantum dots alleviate immune-mediated liver damage
(2014) ACS Nano, 8 (12), pp. 12098-12109.

ABSTRACT: We investigated the effect of large (40 nm) graphene quantum dots (GQDs) in concanavalin A (Con A; 12 mg/kg i.v.)-induced mouse hepatitis, a T cell-mediated liver injury resembling fulminant hepatitis in humans. Intravenously injected GQDs (50 mg/kg) accumulated in liver and reduced Con A-mediated liver damage, as demonstrated by histopathological analysis and a decrease in liver lipid peroxidation and serum levels of liver transaminases. The cleavage of apoptotic markers caspase-3/PARP and mRNA levels of proapoptotic mediators Puma, Noxa, Bax, Bak1, Bim, Apaf1, and p21, as well as LC3-I conversion to autophagosome-Associated LC3-II and expression of autophagy-related (Atg) genes Atg4b, Atg7, Atg12, and beclin-1, were attenuated by GQDs, indicating a decrease in both apoptosis and autophagy in the liver tissue. This was associated with the reduced liver infiltration of immune cells, particularly the T cells producing proinflammatory cytokine IFN-γ, and a decrease in IFN-γ serum levels. In the spleen of GQD-exposed mice, mRNA expression of IFN-γ and its transcription factor T-bet was reduced, while that of the IL-33 ligand ST2 was increased. The hepatoprotective effect of GQDs was less pronounced in ST2-deficient mice, indicating that it might depend on ST2 upregulation. In vitro, GQDs inhibited splenocyte IFN-γ production, reduced the activation of extracellular signal-regulated kinase in macrophage and T cell lines, inhibited macrophage production of the free radical nitric oxide, and reduced its cytotoxicity toward hepatocyte cell line HepG2. Therefore, GQDs alleviate immune-mediated fulminant hepatitis by interfering with T cell and macrophage activation and possibly by exerting a direct hepatoprotective effect. © 2014 American Chemical Society.

Pejić, N.D., Blagojević, S.M., Sarap, N.B., Maksimović, J.P., Anić, S.R., Čupić, Z.D., Kolar-Anić, L.Z.
Perturbations of the dushman reaction with piroxicam: Experimental and model calculations
(2014) Helvetica Chimica Acta, 97 (1), pp. 47-55.

ABSTRACT: Perturbation of the Bray-Liebhafsky non-oscillating subsystem (mixture of KIO3 and H2SO4), i.e., Dushman reaction (DR), by piroxicam (PX), was observed in an open reactor, i.e., in the continuously fed well-stirred tank reactor (CSTR). Monitoring the response of DR to perturbations by different concentrations of PX allows developing a simple procedure for quantitative determination of this analyte in both bulk drug and pharmaceutical preparation (injection). A tentative perturbation mechanism of PX action on the DR matrix, based on a kinetic scheme that was suggested by Agreda et al., is proposed. The PX reactivity in DR has been generally related to the reaction of PX with hypoiodous acid (HIO) present in the matrix. Copyright © 2014 Verlag Helvetica Chimica Acta AG, Zürich.

Stojmenović, M., Bošković, S., Žunić, M., Varela, J.A., Prekajski, M., Matović, B., Mentus, S.
Electrical properties of multidoped ceria
(2014) Ceramics International, 40 (7 PART A), pp. 9285-9292.

ABSTRACT: Multidoped nanosized ceria powders were prepared by either modified glycine nitrate procedure (MGNP) or self-propagating reaction at room temperature (SPRT). As the dopants to CeO2, trivalent rare earth oxides such as Nd2O3, Sm2O3, Gd2O 3, Dy2O3 and Y2O3 were used, with the total molar fraction of 20%. The pressed powder pellets were subjected to the densification by sintering at 1500 °C, in an air atmosphere. A single-phase crystalline form was evidenced by X-ray diffractometry for both sintered materials. By means of complex impedance measurements, the conductivity of the sintered samples was determined as a function of temperature. At 700 °C, the conductivity amounted to 2.19×10-2 and 1.40×10-2 Ω-1 cm-1 for the SPRT and for the MGNP sample, respectively. The corresponding values of activation energies of conductivity amounted to 0.72 (MGNP) and 0.59 (SPRT) eV in the temperature range 550-700 °C. © 2014 Elsevier Ltd and Techna Group S.r.l.

Marković, Z., Crossed D Signorović, J., Dimitrić Marković, J.M., Živić, M., Amić, D.
Investigation of the radical scavenging potency of hydroxybenzoic acids and their carboxylate anions
(2014) Monatshefte fur Chemie, 145 (6), pp. 953-962.

https://doi.org/10.1007/s00706-014-1163-3

ABSTRACT: In this article, the antoxidative mechanisms HAT, SPLET, and SET-PT of the ortho-, meta-, and para-hydroxybenzoic acids and corresponding carboxylate anions with different radicals (·OO-, ·OH, ·OOH, and CH3OO ·) were investigated. For this reason, the ΔH BDE, ΔH IP, and ΔH PA values of the corresponding reactions in different solvents (water, DMSO, pentylethanoate, and benzene) were examined. For this purpose, the M05-2X/6-311++G(d,p) and B3LYP-D2/6-311++G(d,p) theoretical models were applied. Although the B3LYP-D2 method produced lower reaction enthalpy values, both theoretical models exhibited the same trend. It was found that SET-PT is not a favorable reaction path for any hydroxybenzoic acids and their anions with any radicals in any solvents. No anion reacts with -·O2, whereas meta- and para-hydroxybenzoic acids react with -·O2 only in nonpolar solvents. In all other cases, the HAT and SPLET mechanisms are competitive. Which of them is dominant depends on the properties of the acids, anions, radicals, and solvents. Graphical Abstract: [Figure not available: see fulltext.] © 2014 Springer-Verlag Wien.

Ganesan, M.K., Jovanovic, M., Secerov, B., Ignjatovic, M., Bilban, M., Pavle, A., Refaei, A.E., Jung, G., Li, L., Sase, A., Chen, W., Bacic, G., Lubec, G.
Radiation protection from whole-body gamma irradiation (6.7 Gy): Behavioural effects and brain protein-level changes by an aminothiol compound GL2011 in the Wistar rat
(2014) Amino Acids, 46 (7), pp. 1681-1696.

https://doi.org/10.1007/s00726-014-1728-9

ABSTRACT: GL2011 is a naturally occurring thiol compound and a series of thiol compounds have been proposed as radioprotectors. Radioprotective efficacy of a triple intraperitoneal dose of GL2011 of 100 mg/kg body weight of Wistar rats, 30 min prior to and 3 and 6 h

following irradiation (6.7 Gy) was evaluated. Four groups of animals were used, vehicle-treated non-irradiated (VN), GL2011-treated and irradiated (GI), GL2011-treated and non-irradiated (GN) and vehicle-treated and irradiated (VI) (n = 30 per group). The radioprotective efficacy of GL2011 was determined by measuring 28-day survival and intestinal crypt cell survival. Neuroprotection in terms of behaviour was evaluated using the behavioural observational battery, open field test and elevated plus maze paradigm. An RNA microarray was carried out in order to show differences at the RNA level between VI and VN groups. Brain protein changes were identified using a gel-based proteomics method and major brain receptor complex levels were determined by blue-native gels followed by immunoblotting. 28-Day survival rate in VI was 30 %, in GI survival was 93 %, survival of VN and GN was 100 %. Jejunal crypt cell survival was significantly enhanced in GI. Protein-level changes of peroxiredoxin-5, Mn-superoxide dismutase 2, voltage-dependent anion-selective channel protein 1, septin 5 and dopamine D2 receptor complex levels were paralleling radiation damage and protection. Taken together, the findings demonstrate that GL2011 improves survival rates and jejunal crypt survival, provides partial neuroprotection at the behavioural level and modulates proteins known to be involved in protection against oxidative stress-mediated cell damage. © 2014 Springer-Verlag.

Čupić, Z.D., Kolar-Anić, L.Z., Anić, S.R., Maćešić, S.R., Maksimović, J.P., Pavlović, M.S., Milenković, M.C., Bubanja, I.N.M., Greco, E., Furrow, S.D., Cervellati, R.
Regularity of intermittent bursts in Briggs-Rauscher oscillating systems with phenol
(2014) Helvetica Chimica Acta, 97 (3), pp. 321-333.

ABSTRACT: The intermittency or intermittent bursting as the type of dynamic state when two qualitatively different behaviors replace one another randomly during the course of the reaction, although all the control parameters remain constant, is found in the Briggs-Rauscher oscillating system moderated by a very small amount of phenol. Within a range of phenol concentrations, the oscillation amplitude is diminished considerably, and after oscillations cease, they repeat intermittently, giving several bursts of oscillations. For the concentrations used here, the range of phenol concentrations where intermittent bursting oscillations occur in a closed reactor is ca. 1.8×10^{-5} to 3.6×10^{-5} M. Bursting also occurs in an open reactor and can be sustained indefinitely at 5.53×10^{-5} M concentration. The intermittent bursting behavior is robust, and can be achieved at a variety of conditions. Copyright © 2014 Verlag Helvetica Chimica Acta AG, Zürich.

Minić, D.M., Blagojević, V.A., Vasić, M., David, B., Minić, D.M., Pizúrová, N., Žák, T.
Thermally induced crystallization of Fe73.5Cu1Nb 3Si15.5B7 amorphous alloy
(2014) Intermetallics, 45, pp. 53-59.

ABSTRACT: Thermally induced crystallization of Fe73.5Cu1Nb 3Si15.5B7 amorphous alloy occurs in two well-separated stages: the first, around

475 C, corresponds to formation of α-Fe(Si)/Fe3Si and Fe2B phases from the amorphous matrix, while the second, around 625 C, corresponds to formation of Fe 16Nb6Si7 and Fe2Si phases out of the already formed α-Fe(Si)/Fe3Si phase. Mössbauer spectroscopy suggests that the initial crystallization occurs through formation of several intermediate phases leading to the formation of stable α-Fe(Si)/Fe3Si and Fe2B phases, as well as formation of smaller amounts of Fe16Nb6Si7 phase. X-ray diffraction (XRD) and electron microscopy suggest that the presence of Cu and Nb, as well as relatively high Si content in the as-prepared alloy causes inhibition of crystal growth at annealing temperatures below 625 C, meaning that coalescence of smaller crystalline grains is the principal mechanism of crystal growth at higher annealing temperatures. The second stage of crystallization, at higher temperatures, is characterized by appearance of Fe2Si phase and a significant increase in phase content of Fe16Nb 6Si7 phase. Kinetic and thermodynamic parameters for individual steps of crystallization suggest that the steps which occur in the same temperature region share some similarities in mechanism. This is further supported by investigation of dimensionality of crystal growth of individual phases, using both Matusita-Sakka method of analysis of DSC data and texture analysis using XRD data.

Pejin, B., Savic, A.G., Hegedis, A., Karaman, I., Horvatovic, M., Mojovic, M.
A bryozoan species may offer novel antioxidants with anti-carbon-dioxide anion radical activity
(2014) Natural Product Research, 28 (22), pp. 2057-2060.

https://doi.org/10.1080/14786419.2014.921788

ABSTRACT: The antiradical activity of the freshwater bryozoan Hyalinella punctata water extracts (two samples, seasonal collection) was evaluated by using electron paramagnetic resonance spectroscopy against hydroxyl (OH), superoxide anion (CO2-), methoxy (CH2OH), carbon-dioxide anion (CO2-), nitric-oxide (NO) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) radicals. The extracts reduced the production of all tested radicals but to a varying degree. The better activity was observed against CO2- and CH2OH radicals (54 ± 5% and 44 ± 4%, and 58 ± 6% and 22 ± 2%, respectively) than towards DPPH, NO, OH and O2-radicals (59 ± 6% and 1.0 ± 0.1%, 46 ± 5% and 14 ± 1%, 7.0 ± 0.5% and 34 ± 3%, and 33 ± 3% and 0%, respectively). FTIR spectra of the both extracts indicate the presence of cyclic peptides and polypeptides which might be responsible for the observed activity. According to the experimental data obtained, H. punctata water extract may be considered as a novel promising resource of natural products with anti CO2-radical activity. © 2014 Taylor & Francis.

Laher, R.R., Khakoo, M.A., Kuzmanović, M., Antic-Jovanović, A.
Reinvestigation of the electronic transition moment function of the BO B2σ+-X2σ+ band system
(2014) Journal of Quantitative Spectroscopy and Radiative Transfer, 140, pp. 67-74.

https://doi.org/10.1016/j.jqsrt.2014.01.029

ABSTRACT: The relative intensities of nine emission bands associated with the v'=0 and 1 vibrational levels of the B2σ + - X2σ + system of

the BO molecule are measured. The integrated relative intensities of the (0, 0), (0, 1), (1, 0) and (1, 1) bands are measured for the first time in this work. The ratios of observed intensities for bands originating from the same upper vibrational level, together with the Franck-Condon factors, $q_{v'v''}$, and r-centroids, $r_{v'v''}$, based on Rydberg-Klein-Rees potential energy curves, derived from the best available spectroscopic data for the $B2\sigma+$ and $X2\sigma+$ states of $^{11}B^{16}O$ and $^{10}B^{16}O$, are used to reinvestigate the dependence of the electronic transition moment (ETMF), $R_e(r)$, on internuclear distance, r, for the BO $B2\sigma+ - X2\sigma+$ band system. The linear expression $R_e(r_{v'v''})=k(-1+1.393r_{v'v''})$, where k is an arbitrary constant, is derived from our data to describe the measured r-centroid variation of the ETMF for this system over the range 1.23 Å ≤ r ≤ 1.40 Å of internuclear distance. The form of this expression is suitable for directly comparing with previous work, and we find excellent agreement with the BO B-X relative ETMF of Robinson and Nicholls [Intensity measurements on the CO+ comet tail, and the BO α and β molecular band systems. Proc. Phys. Soc. 1960;75:817-25]. Recent radiative-lifetime measurements of the ^{11}BO B state have allowed us to normalize our ETMF to absolute units: $R_e(r_{v'v''})=0.4672r_{v'v''}-0.3354$ (electric dipole moment atomic units), where $r_{v'v''}$ is in Å. © 2014 Elsevier Ltd.

Janković, B., Stopić, S., Bogović, J., Friedrich, B.
Kinetic and thermodynamic investigations of non-isothermal decomposition process of a commercial silver nitrate in an argon atmosphere used as the precursors for ultrasonic spray pyrolysis (USP): The mechanistic approach
(2014) Chemical Engineering and Processing: Process Intensification, 82, pp. 71-87.

https://doi.org/10.1016/j.cep.2014.06.002

ABSTRACT: The non-isothermal decomposition process of commercial silver nitrate used as the precursor for the USP procedure was investigated by simultaneous TGA-DTA measurements at different heating rates, in an argon atmosphere. Detailed kinetic and thermodynamic analyses, with special emphasis on the formation of a complete mechanistic scheme of the process were performed. It was found that the process under study can be described by the acceleratory power law kinetic model (P2), in the range of the extent of conversion (α) values ($0.15 \leq \alpha \leq 0.85$), where the value of the apparent activation energy (Ea) can be considered as the constant ($141.3 kJmol^{-1}$). The kinetic prediction analysis was shown that only the power law kinetic model ($f(\alpha)=2\alpha^{1/2}$) gives the value of Ea which is consistent with the value obtained from the isothermal conditions. The critical temperature (Tc) of decomposition process was determined. The resulting value of Tc was in fairly good agreement with the starting temperature of thermal decomposition of silver oxide (Ag_2O). The thermodynamic functions of decomposition process are calculated by the activated complex theory and showed that the silver-oxygen bond secession can be interpreted as a "slow" stage of the decomposition process. © 2014 Elsevier B.V.

Janković, B., Stopić, S., Güven, A., Friedrich, B.
Kinetic analysis of isothermal decomposition process of zinc leach residue in an inert atmosphere. the estimation of the apparent activation energy distribution

(2014) Mineral Processing and Extractive Metallurgy Review, 35 (4), pp. 239-256.

ABSTRACT: Thermal decomposition of zinc leach residue has been studied in a tubular furnace under a constant nitrogen gas flowing, at four different operating temperatures (600°C, 750°C, 950°C, and 1150°C). Using a detailed kinetic analysis, it was shown that the investigated process can be described by a two-parameter autocatalytic Šesták-Berggren reaction model. It was noted that the apparent activation energy values Ea increase progressively with a degree of conversion, accompanied by the appearance of a convex Arrhenius dependence. This behavior is a characteristic of a system of parallel competing reactions. It was concluded that the investigated isothermal decomposition process is characterized by unusually very low preexponential factor and low values of the apparent activation energy. Based on the derived density distribution function of Ea values, it was concluded that the isothermal decomposition process probably occurs through four reaction steps, where each step is characterized by one parallel reaction. © Taylor and Francis Group, LLC.

Dimitrić Marković, J.M., Milenković, D., Amić, D., Popović-Bijelić, A., Mojović, M., Pašti, I.A., Marković, Z.S.
Energy requirements of the reactions of kaempferol and selected radical species in different media: Towards the prediction of the possible radical scavenging mechanisms
(2014) Structural Chemistry, 25 (6), pp. 1795-1804.

ABSTRACT: Kaempferol, one of the most bioactive plant flavonoids was experimentally and theoretically (at M05-2X/6-311G(d,p) level of theory) investigated for its ability to scavenge potentially, highly damaging hydroxyl and superoxide anion radicals. Relating the obtained hydroxyl radical activity sequence with kaempferol structural features, it could be assumed that C4'-OH functional most probably renders it as hydroxyl radical scavenger, while C5-OH group has more prominent role compared to ortho-hydroxy groups in B ring. However, kaempferol's activity toward superoxide anion radical implicates ortho-hydroxy groups in B ring as more relevant. Theoretical calculations point to HAT and SPLET mechanisms as operative for kaempferol in all solvents under investigations. Graphical Abstract: The present paper aims to provide quantitative tools to thoroughly and comprehensively determine antiradical mechanisms of kaempferol in different media.[Figure not available: see fulltext.] © 2014 Springer Science+Business Media New York.

Dimitrić Marković, J.M., Milenković, D., Amić, D., Mojović, M., Pašti, I., Marković, Z.S.
The preferred radical scavenging mechanisms of fisetin and baicalein towards oxygen-centred radicals in polar protic and polar aprotic solvents
(2014) RSC Advances, 4 (61), pp. 32228-32236.

ABSTRACT: Naturally occurring flavonoid molecules, i.e. fisetin (2-(3,4- dihydroxyphenyl)-3,7-dihydroxychromen-4-one) and baicalein (5,6,7-trihydroxy-2- phenyl-4H-chromen-4-one), have been investigated experimentally and theoretically for their ability to scavenge hydroxyl and superoxide anion radicals. The reaction enthalpies for the reaction of fisetin and baicalein with selected radical species, related to three mechanisms of free radical scavenging activity (HAT, SET-PT and SPLET), are calculated using the M05-2X/6-311+G(d,p) model. The calculated energy requirements indicated the preferred radical scavenging mechanisms in polar protic and aprotic solvents. © the Partner Organisations 2014.

Ganesan, M.K., Jovanovic, M., Secerov, B., Ignjatovic, M., Bilban, M., Andjus, P., Refaei, A.E., Jung, G., Li, L., Sase, A., Chen, W., Bacic, G., Lubec, G.
Erratum: Radiation protection from whole-body gamma irradiation (6.7 Gy): Behavioural effects and brain protein-level changes by an aminothiol compound GL2011 in the Wistar rat (Amino Acids (2014) 46 (1681-1696) DOI 10.1007/s00726-014-1728-9)
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Dorović, J., Marković, J.M.D., Stepanić, V., Begović, N., Amić, D., Marković, Z.
Influence of different free radicals on scavenging potency of gallic acid
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ABSTRACT: The M05-2X/6-311++G(d,p) and B3LYP-D2/6-311++G(d,p) models are used to evaluate scavenging potency of gallic acid. The hydrogen atom transfer (HAT), sequential proton loss electron transfer (SPLET), and single electron transfer followed by proton transfer (SET-PT) mechanisms of gallic acid with some radicals ($\cdot OO-$, $\cdot OH$, and $CH_3OO\cdot$) were investigated using the corresponding thermodynamic quantities: bond dissociation enthalpy (BDE), ionization potential (IP), and proton affinity (PA). Namely, the $\Delta HBDE$, ΔHIP, and ΔHPA values of the corresponding reactions in some solvents (water, DMSO, pentylethanoate, and benzene) are investigated using an implicit solvation model (SMD). An approach based on the reactions enthalpies related to the examined mechanisms is applied. This approach shows that a thermodynamically favored mechanism depends on the polarity of reaction media and properties of free radical reactive species. The most acidic 4-OH group of gallic acid is the active site for radical inactivation. The results of this investigation indicate that the SPLET mechanism can be a favored reaction pathway for all three radicals in all solvents, except for $\cdot OH$ in the aqueous solution. In water, gallic acid can inactivate $\cdot OH$ by the HAT mechanism. © 2014 Springer-Verlag.

Mérian, T., Redon, N., Zujovic, Z., Stanisavljev, D., Wojkiewicz, J.L., Gizdavic-Nikolaidis, M.
Ultra sensitive ammonia sensors based on microwave synthesized nanofibrillar polyanilines
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ABSTRACT: Ultra sensitive ammonia sensors based on microwave (MW) nanofrillar polyaniline (PANI) with ppb sensing range were developed. First PANIs synthesized by classical (CS) and MW assisted methods using different dopants (HCl, H2SO4) and oxidants - (ammonium persulfate (APS) and potassium iodate (KIO3)) were exposed to 1 ppm (700 µg m -3) of ammonia to select the more sensitive. The couple dopant/oxidant (H2SO4/KIO3) leads to PANIs presenting the best responses whatever the method of synthesis used. These selected samples have been further investigated and characterized from a metrological point of view in terms of response, sensitivity, quantification limit, repeatability and reversibility. Compared to CS method, the MW synthesized PANI gives rise to sensor presenting better metrological performances which can be correlated with the physical properties of the samples obtained by using FTIR (Fourier Transform Infrared) and EPR (Electron Paramagnetic Resonance) spectroscopies. In order to further improve the sensitivity of MW PANI at low concentrations of ammonia, conductive composite materials were synthesized using a polyurethane (PU) matrix. The influence of PANI content in the blend on the response to 1 ppm of ammonia was studied and the composite with 38% (in weight) of doped PANI in the matrix presents the largest response. MW PANI composite with 38% (in weight), MW PANI and CS PANI were submitted to a large panel of ammonia concentrations. The composite showed better sensitivity at low concentration of ammonia with a calculated quantification limit of 0.3 ppb while MW PANI provided better responses to high concentrations of ammonia (>5 ppm (3500 µg m-3)). MW PANI in composite provides a way to improve the quantification limit leading to ultra sensitive sensors. © 2014 Elsevier B.V.