

List of Papers Related to Electrochemical Sensing

vs. of 25-Dec-2020; edited by O. S. Wolfbeis

608. Review: Non-Invasive Electrochemical Sensors and Biosensors Targeting Salivary Biomarkers. V. Mani, T. Beduk, W. Khushaim, A. E. Ceylan, S. Timu, O. S. Wolfbeis, K. N. Salama; *Trends Anal. Chem. (TrACh)* (2021), 135, paper # 116164. DOI: 10.1016/j.trac.2020.116164. IF: 9.8.

Abstract: The analysis of salivary markers has grown into a promising non-invasive route for easy, safe, and pain-free biomedical monitoring and has the potential to change the existing way of clinical diagnosis, management, and treatment. Therefore, the interest in saliva as a diagnostic fluid has advanced rapidly in recent years. Advancements in sensing technology, the arrival of novel materials, and the innovative electrode fabrication methods, and accuracy in sampling have recently made significant progress in this field and strongly establishing saliva as a potential alternative fluid resource for traditional blood analysis. The attractive features of saliva analysis are the ease and convenience, samples can be collected readily and more frequently, with less stress on the patient, without piercing the body. In addition, salivary sensing can be easily coupled with in-vitro, in-situ, and POC diagnostic sensors. Saliva contains wide varieties of biomarkers that are useful to detect chronic and infectious diseases. Early-stage detection of cancer, diabetes, Alzheimer's, neurodegenerative diseases, infectious diseases and chronic stress disorders are possible by detecting their corresponding biomarkers levels in saliva.

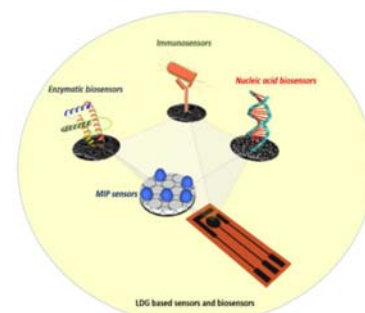
Besides, it is a most appropriate biological fluid for scientific investigations concerning drug abuse ethics. Sialochemistry has promising applicability in toxicology and forensic medicine for analyzing and detecting user drug addiction and alcohol abuse by simply mapping the saliva data. This will enable authorities to make quick decisions on criminal cases, and compare salivary data with blood data to provide more accurate and timely judgments. Electrochemical sensors are the most suitable analytical method for simple, fast and cost-effective analysis of saliva biomarkers in POC. This review, with 520 refs., discusses the scope of electroanalytical techniques in monitoring salivary analytes, broadly divided into three sections; (1) The salivary analytes, their correlation with blood, and their electrochemical detection approaches are presented. (2) The acute and chronic diseases that can be detected by electrochemical salivary analysis are discussed. (3) The salivary drug analysis are discussed. Finally, the technical advancements in making advanced electrochemical sensors and biosensors are discussed.

The table shows representative analytes and their relevant concentration ranges in saliva and blood.

| Analyte | Conc. in Saliva | Conc. in Blood |
|------------|-------------------------|--|
| Glucose | 70 – 88 μM | 3.9 – 7.1 mM |
| Creatinine | 5.3 – 18 μM | 74 – 107 μM |
| Urea | 6.5 – 11 mM | 2.5 to 7.1 mM |
| Uric acid | 199 – 240 μM | 202 – 428 μM (men) 143 – 363 μM (women) |
| Nitrite | 130 – 220 μM | 50 – 100 nM |
| pH value | 6.2 – 7.6 | 7.1 – 7.5 |
| Lactate | 0.1 – 2.5 mM | 0.5 – 2.2 mM (venous) 0.1 – 1.6 mM (arterial) |
| Potassium | 2.6 – 18.5 mM | 3.6 – 5.2 mM |

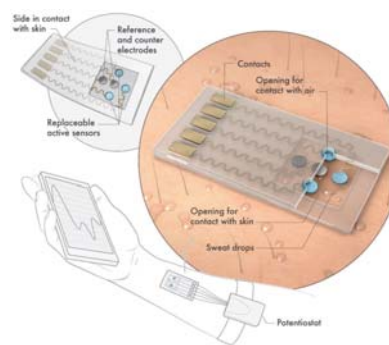
606. Review: Electrochemical Sensors and Biosensors Using Laser-Derived Graphene: A Comprehensive Review. A. A. Lahcen, S. Rauf, T. Beduk, C. Durmus, A. Aljedaibi, S. Timur, H. N. Alshareef, A. Amine, O. S. Wolfbeis, K. N. Salama; *Biosensors & Bioelectronics* (2020) 168, 112565. IF: 10.3.

Abstract: Laser-derived graphene (LDG) technology is gaining attention as a novel platform for electrochemical sensors and biosensors. Compared to established methods for graphene synthesis, LDG provides many advantages such as cost-effectiveness, fast electron mobility, mask free and green synthesis, good electrical conductivity, porosity, mechanical stability and large surface area. This review discusses, in a critical way, recent advancements in this field. First, we focus on the fabrication and doping of LDG platforms using different strategies. Next, the techniques for the modification of LDG sensors using nanomaterials, conducting polymers, biological receptors and artificial receptors are presented. We then describe the advances achieved for various LDG sensing and biosensing schemes and their applications in the fields of environmental monitoring, food safety, and clinical diagnosis. Finally, the drawbacks and limitations of LDG based biosensors are addressed, and future trends are outlined.



605. A MXene-Based Wearable Biosensor System for High-Performance In-Vitro Perspiration Analysis. Y. Lei, W. Zhao; Y. Zhang, Q. Jiang, J. He, A. J. Baeumner, O. S. Wolfbeis, Z. L. Wang, K. N. Salama, H. N. Alshareef, *Small* (2019) 1191190. DOI: 10.1002/sml.201901190. IF: 9.6.

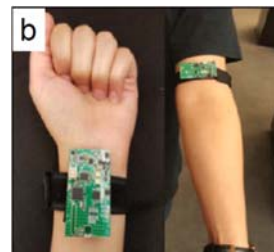
Abstract: Wearable electrochemical biosensors for sweat analysis present a promising means for noninvasive biomarker monitoring. A stretchable, wearable, and modular multifunctional biosensor is developed, incorporating a novel MXene/Prussian blue (Ti₃C₂T_x/PB) composite designed for durable and sensitive detection of biomarkers (e.g., glucose and lactate) in sweat. Furthermore, an implemented solid-liquid-air three-phase interface design leads to superior sensor performance and stability. Typical electrochemical sensitivities of 35.3 $\mu\text{A mm}^{-1} \text{cm}^{-2}$ for glucose and 11.4 $\mu\text{A mm}^{-1} \text{cm}^{-2}$ for lactate are achieved using artificial sweat. During in vitro perspiration monitoring of human subjects, the signals (glucose and lactate level) can be measured simultaneously with high sensitivity and good repeatability. This approach represents an important step toward the realization of ultrasensitive enzymatic wearable biosensors for personalized health monitoring.



604. KAUSTat: A Wireless, Wearable, Open-Source Potentiostat for Electrochemical Measurements. R. Ahmad, S. G. Surya, J. B. Sales, H. Mkaouar, S. Y. C. Catunda, D. R. Belfort, Y. Lei, Z. L. Wang, A. J. Baeumner, O. S. Wolfbeis, H. N. Alshareef, K. N. Salama. *2019 IEEE Sensors (Montreal, Canada; 27-30 Oct.*

2019), pp. 1-4. DOI: 10.1109/SENSORS43011.2019.8956815.

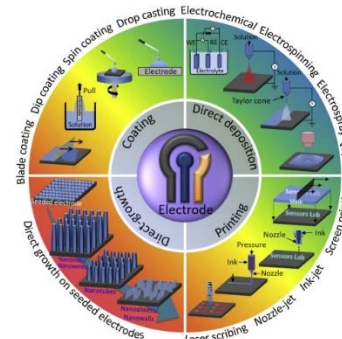
Abstract: Potentiostats used in laboratories are heavy, non-portable, and expensive. To fill this void, we introduce KAUSTat, a wireless, wearable, open-source potentiostat. The KAUSTat device interfaces with a smartphone to generate cyclic voltammetry curves using a Bluetooth Low Energy (BLE) protocol. Experiments with buffer and hexacyanoferrate solutions were conducted to assess the efficiency of the device. The results generated by KAUSTat are in agreement with those of the commercial potentiostat Emstat. Considering wireless and wearable features of KAUSTat, it represents a convenient portable device for on-site sensing with low-power requirements.



601. Review: Deposition of Nanomaterials: A Crucial Step in Biosensor Fabrication.

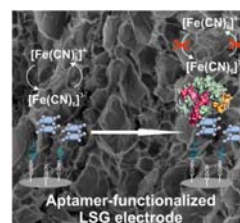
R. Ahmad, O. S. Wolfbeis, Y.-B. Hahn, H. Alshareef, L. Torsi, K. N. Salama. *Materials Today Comm.*, (2018), 17, 289-321. DOI: 10.1016/j.mtcomm.2018.09.024. IF: 9.9.

Abstract: Biosensor development includes the deposition of nanomaterials onto a sensor surface. This is a crucial step for obtaining improved performance. Various methods have been used to create a successful matrix of nanomaterials that warrant proper contact between the material and sensor surface. The purpose of nanomaterial deposition is to provide a high surface area to improve the performance of biosensors by supporting the stable immobilization of enzymes in a more significant quantity as well as enhancing the catalytic or bioaffinity features. In this review (with 431 refs.), we summarize the methods used for nanomaterial deposition onto an electrode surface for efficient biosensor fabrication. An optimized nanomaterial deposition method is also crucial for the mechanical stability and fabrication reproducibility of electrodes when designing a suitable biosensing device. In addition, we discuss the challenges faced during biosensor application as well as prospects for superior deposition methods.



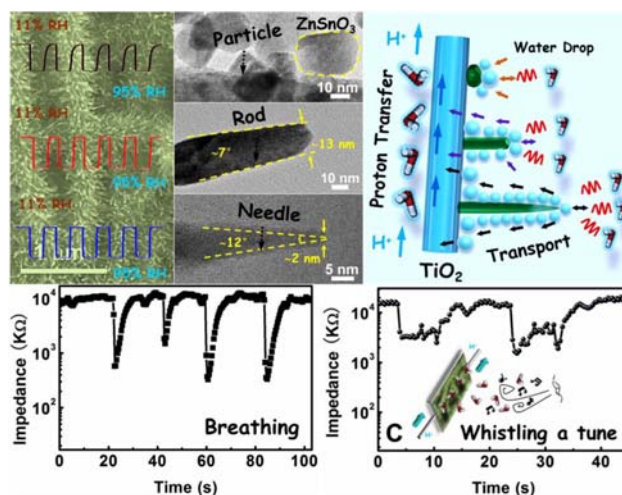
598. Laser-Scribed Graphene Electrodes for Aptamer-Based Biosensing. C. Fenzl, P. Nayak, T. Hirsch, O. S. Wolfbeis, H. N. Alshareef, A. J. Baeumner; *ACS Sensors* (2017), 2, 616-620. DOI: 10.1021/acssensors.7b00066. IF: 7.7.

Abstract: Graphene as a transducer material has produced some of the best-performing sensing approaches to date opening the door toward integrated miniaturized all-carbon point-of-care devices. Addressing this opportunity, laser-scribed graphene (LSG) electrodes are demonstrated here as highly sensitive and reliable biosensor transducers in blood serum analysis. These flexible electrodes with large electrochemical surface were fabricated using a direct-write laser process on polyimide foils. A universal immobilization approach is established by anchoring 1-pyrenebutyric acid to LSG and subsequently covalently attaching an aptamer against the coagulation factor thrombin as an exemplary bioreceptor to the carboxy groups. The resulting biosensor displays an extremely low detection limit of 1 pM in buffer, and of 5 pM in serum.



589. Rational Tailoring of ZnSnO₃-TiO₂ Heterojunctions with Bioinspired Surface Wettability for High-Performance Humidity Nanosensors. Z. Zhang, J. Huang, B. Dong, Q. Yuan, Y. He, O. S. Wolfbeis. *Nanoscale* (2015), 7, 4149-4155. DOI: 10.1039/c4nr07559e. IF: 7.4

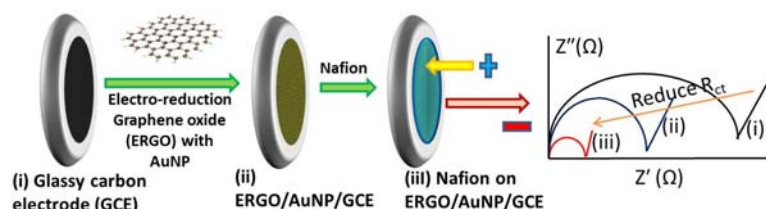
Abstract: We have developed a novel kind of branched heterostructures by hydrothermal growth of the ZnSnO₃ nanostructures on TiO₂ electrospun nanofibers, and demonstrate enhanced sensing of relative humidity (RH) through sequential tailoring ZnSnO₃ nanostructures inspired by the cactus. Combining with the first-principles calculations, it is deduced that the quantity of adsorbed water molecules can be increased on the ZnSnO₃-TiO₂ heterojunction surface by reducing the surface potential barrier. The bioinspired ZnSnO₃ nanoneedles, acting like branches on the heterostructures, can further boost their adsorption abilities for water molecules via a water-collection process. The adsorbed water molecules at the tips of the ZnSnO₃ nanoneedles quickly desorb at a lower humidity environment due to the small area of the tips (1.5 to 2.5 nm). Thus, the optimal ZnSnO₃-TiO₂ heterostructures exhibit fast response and recovery times (of ~2.5 s and ~3 s, respectively). Its good sensitivity may enable it to detect tiny fluctuations in the RH surrounding any high-precision instrumentation.



585. Review: Nanomaterial-based Electrochemical Sensing of Neurological Drugs and Neurotransmitters. B. J. Sanghavi, O. S. Wolfbeis, T. Hirsch, N. S. Swami; *Microchim. Acta* (2015), 182, 1-41. DOI: 10.1007/s00604-014-1308-4. Open access. IF: 3.7.

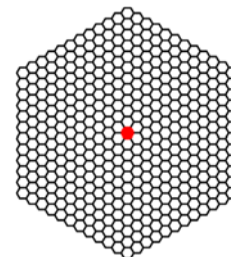
Abstract: Nanomaterial-modified detection systems represent a chief driver towards the adoption of electrochemical methods, since nanomaterials enable functional tunability, ability to self-assemble, and novel electrical, optical and catalytic properties that emerge at this scale. This results in tremendous gains in terms of sensitivity, selectivity and versatility. We review the electrochemical methods and mechanisms that may be applied in the detection of neurological drugs. We focus on understanding how specific nano-sized modifiers may be applied to influence the electron transfer event to result in gains in sensitivity, selectivity and versatility of the detection system. Specific sections are dedicated to electrodes based on the carbon materials, supporting electrolytes, and on electrochemical detection paradigms for neurological drugs and neurotransmitters. We finally discuss emerging trends and future challenges such as the development of strategies for simultaneous detection of multiple targets with high spatial and temporal resolutions, the integration of microfluidic strategies for analyte preconcentration, the real-time monitoring of neurotransmitter secretions from

active cell cultures under electro- and chemotactic cues, aptamer-based biosensors, and the miniaturization of the sensing system for detection in small sample volumes and for enabling cost savings due to manufacturing scale-up. The Supp. Information includes a list of the key properties of the analytes, viz. pK_a values, half-life of drugs and their electro-chemical mechanisms. It also defines analytical figures of merit of the drugs and neurotransmitters. The review contains 198 references in the main manuscript and 207 references in the Supp. Information.



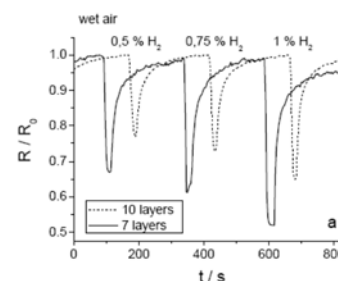
549. Review: Graphenes in Chemical Sensors and Biosensors. S. Kochmann, Th. Hirsch, O.S. Wolfbeis; *Trends Anal. Chem.* (2012), 39, 87-113. DOI: 10.1016/j.trac.2012.06.004. IF: 6.3.

Abstract: This review covers the current state of the art of using graphenes in electrochemical and optical chemical sensors and biosensors. We first discuss the types of graphenes, graphene oxides, and the like, and also give a definition for each. This is followed by a section on the use of nonmodified materials ("plain graphenes") in mainly electrochemical and optical chemical sensors and (bio)sensors. The next section summarizes the various kinds of sensors based on composite materials containing graphenes, with subsections on electro-chemical, field effect transistor-based, fluorescent, chemi-luminescent and colorimetric sensors. It is shown that the use of graphenes alone or in composite form can improve the performance of chemical sensors and biosensors, in particular with respect to the dynamic ranges, lower limits of detection, selectivity and size of instrumentation. The review is based on ~270 references from the time period between 2007 and 2012.



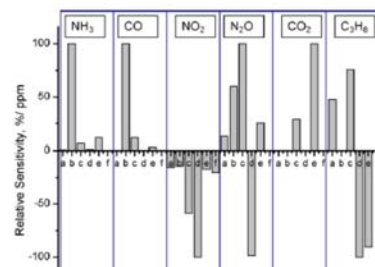
520. Hydrogen Sensor Based on a Graphene-Palladium Nanocomposite. U. Lange, T. Hirsch, V. M. Mirsky, O. S. Wolfbeis; *Electrochim. Acta* (2010), 56, 3707-3712. DOI: 10.1016/j.electacta.2010.10.078. IF: 3.6.

Abstract: We describe a sensor for detecting hydrogen at levels from 0.5 to 1% in synthetic air. Pure graphene is poorly sensitive to hydrogen, but incorporation of PdNPs increases its sensitivity by more than an order of magnitude. The effects of hydrogen, nitrogen dioxide and humidity were studied. The sensor regeneration was accelerated essentially in humid air. The sensitivity of the nanocomposite depends on the number of bilayers of graphene-PdNPs prepared via layer-by-layer deposition on gold electrodes. The material was characterized by absorption spectroscopy, scanning electron and Raman spectroscopy, and surface plasmon resonance. Cyclic voltammetry demonstrated the presence of electrocatalytic centers in the palladium-decorated graphene.



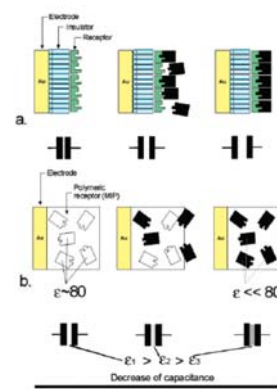
490. Gas Sensing Properties of Electrically Conductive Copper(I) Compounds at Elevated Temperatures. B. Wolpert, O. S. Wolfbeis, V. M. Mirsky; *Sens. Actuat. B* (2009), 142B, 446-450. DOI: 10.1016/j.snb.2008.06.047. IF: 3.1.

Abstract: The electrical conductance at 240 °C of a number of copper(I) compounds including halides, tellurides, phosphides, and of NiO was studied with respect to its response to ammonia, nitrogen dioxide, nitrous oxide, carbon monoxide, carbon dioxide, and propane. Analytical sensitivity and kinetic parameters were compared quantitatively. The high diversity of sensitivity patterns makes these compounds promising candidates for use in sensor arrays. Principal component analysis of the data obtained with a virtual sensor array enabled highly selective sensing of five of the six analytes studied using only two principle components.



450. Capacitive Detection in Ultrathin Chemosensors Prepared by Molecularly Imprinted Grafting Photopolymerization. T. L. Delaney, D. Zimin, M. Rahm, D. Weiss, O. S. Wolfbeis, V. M. Mirsky; *Anal. Chem.* (2007), 79, 3220-3225. DOI: 10.1021/ac062143v. IF: 5.7.

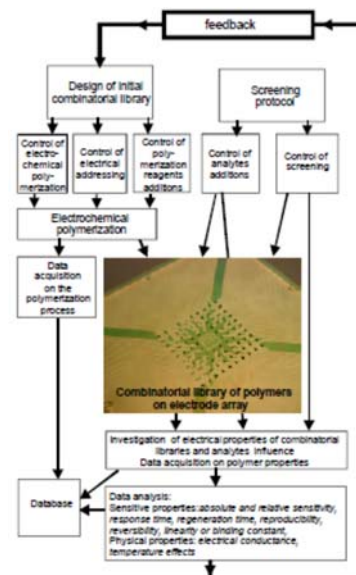
Abstract: The usual applications of capacitive detection in chemo- and biosensors are based on changes in effective thickness of insulating layers due to adsorption of analyte onto receptors. Ultrathin chemosensors based on molecularly imprinted polymerization enable a realization of another capacitive approach that exploits changes in electrical capacitance due to modification of the dielectric constant of the polymer. Such chemosensors were prepared by photografted molecularly imprinted polymerization on the surface of gold electrodes. An adsorbed layer of hydrophobic photo-initiator (benzophenone) provided grafted polymerization on the surface of the alkanethiol-modified gold electrode. The chemosensors were characterized by cyclic voltammetry, impedance spectroscopy, and scanning electron and atomic force microscopy. Binding of analyte was detected by measurements of electrical capacitance. The results indicate a decrease of the dielectric constant of the polymer layer due to analyte binding up to 20%. The figure symbolizes that signals of capacitive sensors can be caused by (a) changes in the thickness of the total insulating layer, and (b) by changes of the dielectric constant of the insulating layer.



425. Complete System for Combinatorial Synthesis and Functional Investigation of Conductive Polymers. V. M. Mirsky, V. Kulikov, O. S. Wolfbeis; *Polym. Mater. Sci. Eng. Preprints (Am. Chem. Soc.)* (2005), 93, 1053. Web: <https://opus4.kobv.de/opus4-UBICO/frontdoor/index/index/docId/18148> ; <https://epub.uni-regensburg.de/20301/>

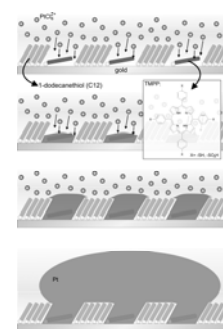
Abstract: We describe here an automated high-throughput system to perform automated electropolymerization as used in various fields of science and technology. It allows polymer layers of controlled thickness to be prepared, and to form multilayer systems. The method is compatible with inorganic electroplating. Applications of electropolymerization include fabrication of chemical sensors and biosensors, deposition of corrosion protective coatings, development of organic electronic devices and electrochromic windows.

The graph shows the complete system for combinatorial electropolymerization and high-throughput characterization. Also shown is the protocol (work-flow) for functional characterization of the resulting materials.



416. Size-Controlled Electrochemical Synthesis of Metal Nanoparticles on Monomolecular Templates, T. Hirsch, M. Zharnikov, A. Shaporenko, J. Stahl, D. Weiss, O. S. Wolfbeis, V. M. Mirsky; *Angew. Chem.* (2005), 44, 6775-6778. DOI: 10.1002/anie.200500912. IF: 10.3.

Abstract: A new technique is described for preparation of metallic nanoparticles on electrode surfaces which does not require the use of STM. The method is based on the reduction of metals on nanoelectrodes formed by the recently developed spreader-bar technique. A variation of the reduction current provides a simple way to control the size of nanoparticles. This novel nanoelectrochemical approach was tested with deposition of platinum and copper but we do not see any principal limitation for its extension to other conductive and semiconductive materials such as different metals, electrochemically synthesized polymers, nanocomposites and others. Also the size of formed nanoparticles which is in our work between 20 and 1000 nm can probably be reduced.



408. High-Throughput Analysis of Bulk and Contact Conductance of Polymer Layers on Electrodes. V. Kulikov, V. M. Mirsky, T. Delaney, D. Donoval, A. W. Koch, O. S. Wolfbeis; *Measurement Sci. Technol.* (2005), 16, 95-99. DOI: 10.1088/0957-0233/16/1/013. IF: 1.2.

Abstract: An approach for high-throughput analysis of bulk and contact conductance of polymer layers is described and evaluated. The approach, based on simultaneous two- and four-point conductance measurements, was realized as a high-throughput method and applied for investigation of conductive polymers on an array of interdigital platinum electrodes. Several examples demonstrate distinctive influence of combinatorially varied conditions of polymer synthesis (polymerization charge, content of copolymers) as well as chemical treatment of the synthesized polymers in bulk and contact resistance of metal/polymer/metal systems. The technique can be widely applied to material research for investigation of bulk and contact electrical properties.

391. Enantioselective Artificial Receptors Formed by the Spreader-Bar Technique. M. I. Prodromidis, Th. Hirsch, V. M. Mirsky, O. S. Wolfbeis; *Electroanalysis* 15 (2003) 1795-1798. DOI: 10.1002/elan.200302756. IF: 2.4.

Abstract: Chiroselective binding sites have been created on thin gold films by application of the spreader-bar approach. Impedometric techniques and surface plasmon resonance were applied to detect binding. (R)-(+)-1,1'-Binaphthyl-2,2'-diol (R-BNOH) and (S)-(-)-1,1'-binaphthyl-2,2'-diol (S-BNOH) were used as model analytes. The artificial receptors were prepared by co-adsorption of 16-mercaptohexadecane (matrix) with a thiol-modified chiral selector (template). The conjugates of D,L-thioctic acid and (R)-(+)- or (S)-(-)-1,1'-binaphthyl-2,2'-diamine were used as templates. Different concentration ratios of the matrix and template were tested. No chiral selectivity of surfaces formed by either the matrix or the template alone was observed. The use of alkylthiols shorter than 16-mercaptohexadecane led to the formation of surfaces with no chiral selectivity. The gold electrodes coated by the spreader-bar technique displayed an enantioselectivity of up to 4.7 or up to 2.5 as measured by the capacitive and SPR methods, respectively.

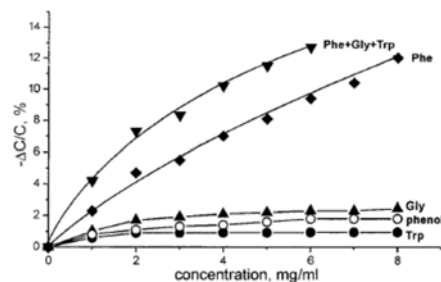
352. Impedometric Herbicide Chemosensors Based on Molecularly Imprinted Polymers. T. Panasyuk-Delaney, V. M. Mirsky, M. Ulbricht, O. S. Wolfbeis; *Anal. Chim. Acta* 435 (2001) 157-162. DOI: 10.1016/S0003-2670(00)01280-0. IF: 2.9.

Abstract: The technique of grafting polymerization has been used for preparation of thin films of molecularly imprinting polymers on the surface of polypropylene membranes and on hydrophobized gold electrodes. The herbicide desmetryn was used as a template. The solid supports used were hydrophobic, while the polymer was hydrophilic. The adsorbed layer of benzophenone, irradiated by UV-light, initiated a radical polymerization near the surface. Polymer films were characterized by weighing, contact angle measurements and impedance spectroscopy. The electrodes coated with the molecularly imprinted polymers displayed fairly specific binding of desmetryn, as detected by the decrease in the capacitance of the electrode. Only small capacitive effects were observed on addition of terbumeton or atrazine, while metribuzine displayed a decrease in capacitance similar to that of desmetryn.

328. Electro-Polymerized Molecularly Imprinted Polymers as Receptor Layers in Capacitive Chemical Sensors. T. L. Panasyuk, V. M. Mirsky, S. A. Piletsky, O. S. Wolfbeis; *Anal. Chem.* **71** (1999) 4609-4613. DOI:

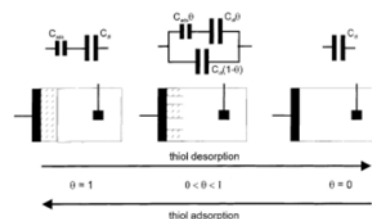
10.1021/ac9903196

Abstract: The first application of molecularly imprinted polymers to chemical sensors with capacitive detection is described. The sensitive layer was prepared by electropolymerization of phenol on gold electrodes in the presence of the template (phenylalanine). The insulating properties of the polymer layer were studied by electrochemical impedance spectroscopy. Electrical leakages through the polymer layer were suppressed by deposition of a self-assembled monolayer of mercaptophenol before polymerization and of alkanethiol after polymerization. At the final stage of the sensor preparation, the template was removed. The multi-layer system obtained displayed a decrease in electrical capacitance on addition of phenylalanine.



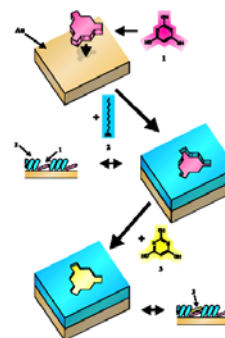
323. Electrical Control of Alkanethiols Self-Assembly on a Gold Surface as an Approach for Preparation of Micro-Electrode Arrays. M. Riepl, V. M. Mirsky, O. S. Wolfbeis; *Microchim. Acta* **131** (1999) 29-34. DOI: 10.1007/s006040050006

Abstract: It is shown by capacitive monitoring that the self-assembly of alkanethiols on gold electrodes and desorption of these self-assembled monolayers from the electrodes are controlled by the electrode potential. At neutral pH, chemical adsorption of alkanethiols was observed at an electrode potential of +300mV vs SCE, but only physical adsorption was detected when the electrode potential was -1400 mV vs SCE. At electrode potentials between these values (-300mV, -600 mV), chemical adsorption of alkanethiols occurred, but the alkanethiol monolayers were not stable in the absence of the alkanethiol in the bulk solution and were desorbed from the gold electrode. The desorption rate was higher at more negative electrode potentials. These results can be used in designing methods for electrically addressable immobilization of different receptors on (micro)electrode arrays. This has been demonstrated by deposition of two different types of alkanethiols onto a two-electrode array.



316. A Spreader-Bar Approach to Molecular Architecture: Formation of Stable Artificial Chemoreceptors. V. M. Mirsky, Th. Hirsch, S. A. Piletsky, O. S. Wolfbeis; *Angew. Chem. Intl. Ed. Engl.* **38** (1999) 1108-1110. DOI: 10.1002/(SICI)1521-3773(19990419)38:8<1108::AID-ANIE1108>3.0.CO;2-C

Abstract: We describe a spreader-bar approach that allows for the first time noncross-linked monolayers to be obtained, whose structure can not be distorted by lateral diffusion. An artificial interface with a high affinity for barbituric acid (a starting material for many pharmaceuticals) was created by co-adsorption of thiobarbituric acid (the template) and dodecanethiol (the matrix) onto a gold substrate. This process leads to the formation of binding sites with a structure complementary to that of thiobarbituric acid. Binding of barbituric acid and of other species to the resp. surface was detected by capacitance measurements. A high selectivity of this artificial chemo-receptor for barbituric acid was observed.



312. A Minimal Binding Domain of the Low Density Lipoprotein Receptor Family, T. M. Bajari, K. A. Lindstedt, M. Riepl, V. M. Mirsky, J. Nimpf, O. S. Wolfbeis, H. A. Dresel, E. K. F. Bautz, W. J. Schneider, *Biol. Chem.* **379** (1998) 1053-1062. DOI: 10.1515/bchm.1998.379.8-9.1053

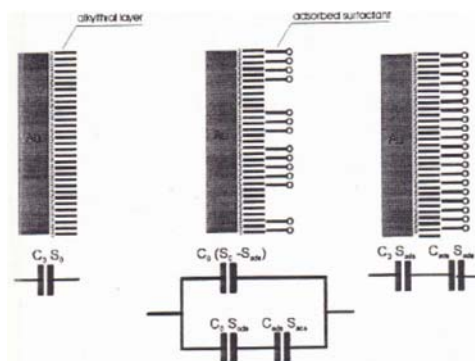
Abstract: As more relatives of the low density lipoprotein receptor (LDLR) are discovered, defining their minimal binding domain(s) becomes a challenge. Here we have chosen the multifunctional chicken oocyte receptor for yolk deposition (termed LR8), and the pan-receptor ligand, receptor associated protein (RAP), as model systems to characterize a minireceptor using the phage display approach. Displayed fragments derived from the entire 819 residue LR8 molecule, followed by selection via panning on RAP, led to the definition of an 80 residue stretch LR8 minireceptor. It contains 12 cysteines, and represents parts of the second, the entire third, and parts of the fourth, of the eight clustered 'ligand binding repeats' in LR8; only two of the eight stretches of negatively charged residues of LR8, i.e., EDGSDE and DSGEDEE, are present. The LR8-derived minireceptor provided a RAP-responsive surface when covalently coupled to the surface of a gold electrode. In addition to its use in defining minimal binding domains, the phage display approach provides powerful tools for dissection, and consequently, manipulation, of the function of receptors.

304. Capacitive Study of Self-Assembled Monolayers: Surface Charge Effects and Kinetics of Surfactant Adsorption, R. Schweiss, V. M. Mirsky, O. S. Wolfbeis; *Mat. Sci. Forum* **287/288** (1998) 427-430 (TransTech Publ., Winterthur, CH). ISSN 0255-5476. DOI: 10.4028/www.scientific.net/MSF.287-288.427

Abstract: Adsorption and desorption kinetics of different surfactants onto/from the surface of gold electrodes covered by self-assembled monolayers of 1-octadecanethiol were monitored in aqueous solutions by means of capacitive measurements. The formation of an adsorbed layer with a specific capacitance C_{ads} and an area of S_{ads} leads to a decrease in the electrode capacitance C_0 for the value ΔC according to

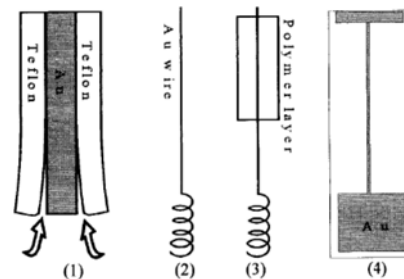
$$\frac{\Delta C}{C} = \frac{S_{ads}}{S_0} \frac{c_0}{c_0 + c_{ads}}$$

The effects of temperature, surfactant concentration and of the surfactants hydrophobic chain length were studied. A linear dependence between the initial slope of the adsorption kinetics and surfactant concentration was observed. This effect can be used for analytical determination of surfactants. The adsorption kinetics suggests a fractal geometry of the surfactants adsorption. The influence of pH value and ionic strength on the capacitance of gold electrodes covered by end-terminated alkylthiols was studied. The curves obtained depend on the ionic strength and have minima near the pK_a of the terminal group.



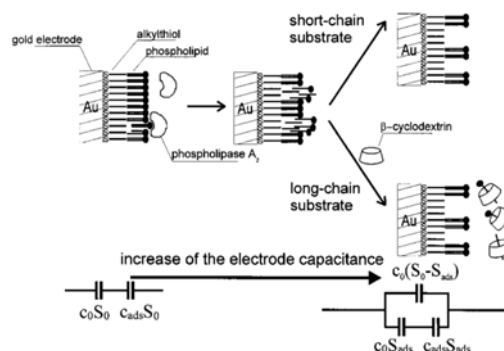
303. Thin Film Electrodes for Capacitive Chemo-, Biosensors: Optimization of the Electrode Geometry, V. M. Mirsky, M. Riepl, Ch. Krause, I. Novotny, M. Splonskowski, V. Rehacek, V. Tvarozek, H. Hummel, O. S. Wolfbeis; *Mat. Sci. Forum* **287/288** (1998) 423-426 (TransTech Publ., Winterthur, CH). ISSN 0255-5476. DOI: 10.4028/www.scientific.net/MSF.287-288.423

Abstract: Different types of electrodes for capacitive chemical sensors and biosensors were investigated. It is found that precise measurements are impossible if the electrodes have a traditional geometry because of a meniscus artifact. The figure shows the different electrode geometries: (1) Thick gold wire coated with a Teflon tube. (2) Thin gold wire. (3) Thin gold wire partially coated with a polymer layer. (4) Thin film gold electrode.



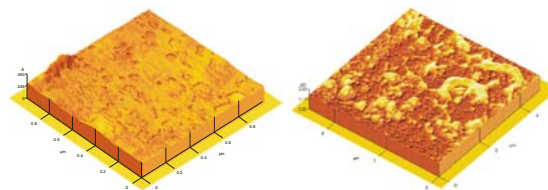
298. Capacitive Approach to Determine Phospholipase A2 Activity towards Natural Substrates, V. M. Mirsky, M. Mass, Ch. Krause, O. S. Wolfbeis; *Anal. Chem. (Wash.)* **70** (1998) 3674-3678. DOI: 10.1021/ac980102w

Abstract: A capacitive approach has been employed to develop a novel method to determine phospholipase activity. The sensing electrodes have a structure of the type Au/S(CH₂)₁₇CH₃/substrate/electrolyte. Hydrolysis of the substrate, mediated by phospholipase A₂, leads to the formation of watersoluble products from the insoluble substrate. This results in desorption of these products into aqueous phase and corresponding increase of the electrode capacitance. The requirement of high water solubility of the reaction products can be achieved in two ways. In the first, short-chain phospholipids are used as the substrate, in which case, water-soluble products are formed and no additional reagents are required to promote desorption of these products. The sensors prepared by this strategy provide sensitive qualitative detection of phospholipases. The second way is based on the use of a water-soluble acceptor (for example cyclodextrin) to solubilize the products of hydrolysis. It allows semiquantitative detection of phospholipase activity toward long-chain natural substrates. The reaction kinetics for this case was found to be monoexponential and linearly dependent on the phospholipase concentration. The detection limit of this method, as tested with phospholipase A₂ from bee venom and soy bean lecithin as the substrate, is 0.5 ng/mL (500 i-units/mL).



283. Capacitive Monitoring of Protein Immobilization and Antigen-Antibody Reactions on Mono-molecular Alkylthiol Films on Gold Electrodes, V. M. Mirsky, M. Riepl & O. S. Wolfbeis; *Biosensors & Bioelectron.* **12** (1997) 977-989. DOI: 10.1016/S0956-5663(97)00053-5

Abstract: Self-assembled monolayers of omega-mercaptohexadecanoic acid on gold electrodes are stable at neutral pH and display purely capacitive behavior at frequencies of around 20 Hz. Covalent immobilization of anti-HSA on the activated surface was monitored by capacitive analysis. Subsequent binding of the antigen (HSA) led to a decrease of the capacitance, thus providing a means for sensitive quantitation of HSA. The limit of detection was as low as 15 nM (1mg/L). The figure shows AFM images of a HS-C16-carboxy acid covered gold electrode (1.0 μm x 1.0 μm) before (left) and after immobilization of HSA (right; size 5.0 μm x 5.0 μm).



..end