

5th ECHEMS Meeting

Oral Presentations

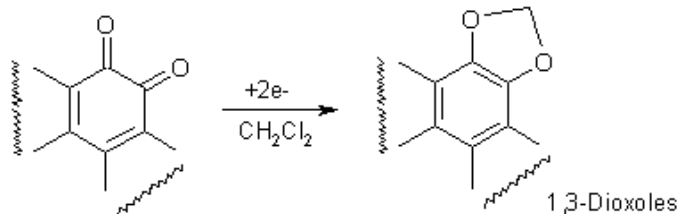
Interesting Products in the Cathodic Reduction of Dicarbonyl Compounds

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The cathodic reduction of 1,2-quinones and other dicarbonyl compounds is presented to produce very interesting and useful organic structures through an electrochemical pathway which depends on the nature of the solvent employed.

As indicated in the scheme, 1,2-quinones in dichloromethane/ Et_4NCl as solvent-supporting-electrolyte produce the corresponding 1,3-Dioxoles¹ in good yield.

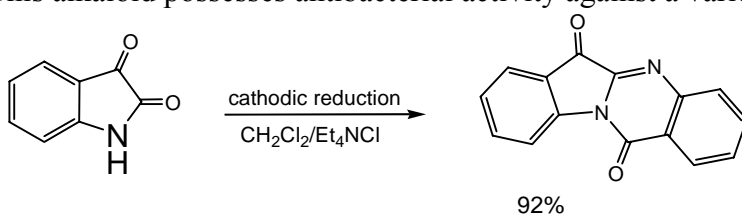


However, the same reaction in 1,2-dichloroethane/ Et_4NCl afford 1,4-Dioxins.²

When Benzil and Furil are reduced under potentiostatic conditions carboxylic acids are obtained.³

An electrochemically induced Henry reaction produced β -nitroalcohols from Acenaphthenequinone, N-Methyl-Isatin or 9,10-Phenanthrene quinone.⁴

The electroreduction of Isatin in dichloromethane/ Et_4NCl afforded Tryptanthrin⁵ in 92% yield. This alkaloid possesses antibacterial activity against a variety of pathogenic agent.



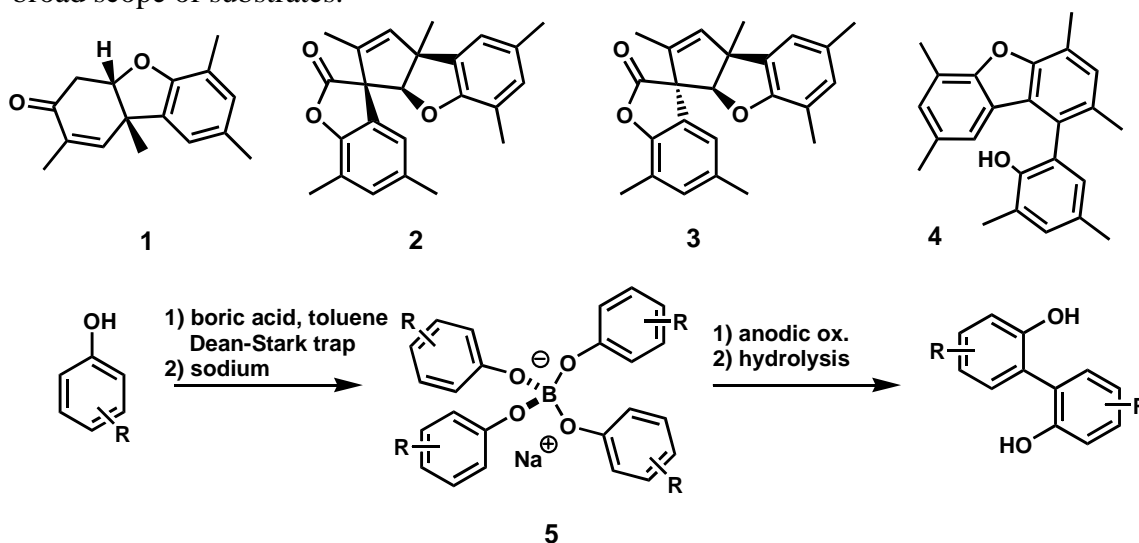
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Novel Anodic Concepts for the selective Phenol Coupling Reaction

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The oxidative phenol coupling reaction of phenols exhibiting simple methyl substituents can be difficult since several by-products occur. Such a challenging substrate is 2,4-dimethylphenol. We studied the electrochemical access to the *ortho*-coupled dehydrodimer. Anodic treatment in a basic electrolyte supports the formation of a molecular architecture called Pummerer's ketone (**1**). Employing a two-step sequence involving anodic conversion of 2,4-dimethylphenol to a preliminary substrate and different workup protocols yields exclusively and diastereoselectively in the polycyclic architectures (**2-4**). The selective *ortho*-coupling reaction was achieved by two ways which will be outlined in detail: On one hand, a borate template **5** can be used. The tetraphenoxo borates can be easily made in large scale. Due to the ionic nature of **5** no supporting electrolyte is required. This methodology can be applied to several related phenolic substrates. On the other hand, 2,4-dimethyl phenol can be directly converted utilizing boron doped diamond anodes. Surprisingly, the electrochemical transformation does not destruct or mineralize the substrate. Using fluorinated mediators allow the conversion of a broad scope of substrates.



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Electroreduction of trichloroacetyl esters of aldols

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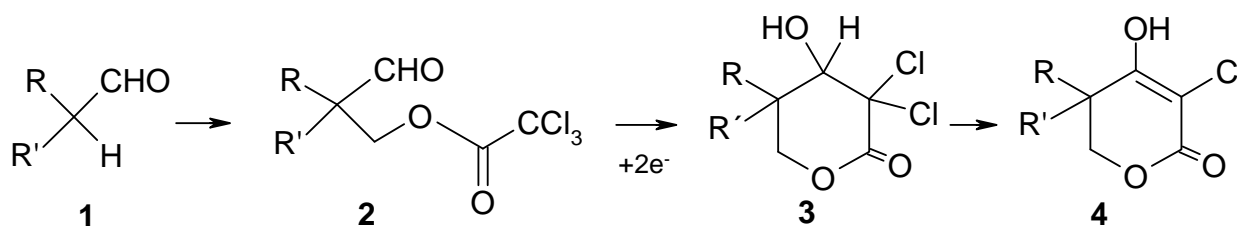
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Key words: aldol trichloroacetates, cathodic reduction, δ -lactones

Abstract:

Previous papers of our research group had described the electrosynthesis of γ - and δ -lactones by anodic oxidation of several starting materials (1, 2). There are also in the literature descriptions of synthesis of lactones by using cathodic reduction (3, 4).

The electroreduction of the carbon-halogen bond has been one of the best studied topics in the research group of Prof. Barba. Thus, new coumarins have been obtained by reduction of trichloroacetyl esters of *o*-hydroxyketones in aprotic media(5). Following with this process, we report in the present work the synthesis of new substituted α,α -dichloro- β -hydroxy- and α -chloro- β -hydroxy- α,β -insaturated δ -lactones by cathodic reduction at a controlled potential of trichloroacetyl esters of aldols in dichloromethane, tetraethylammonium chloride.



Synthesis of trichloroacetyl esters **2**, mechanism of the process and yield of the obtained compounds are discussed.

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Electrochemical microscopy at variable temperatures

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Many interfacial processes are of electrochemical nature or involve electrochemical steps. Electrochemical microscopy (SECM) is especially suited for studying such processes, because manifold localized electrochemical techniques can be implemented. Of great advantage is the fact, that the experimental conditions can be varied at a huge extent to adapt them to the particular problem, as long as at least one of the involved phases is liquid. This property allows the examination of surfaces under realistic conditions.

Applications of SECM include corrosion processes at surfaces, the investigation of new materials with catalytic activity, the local activity of biologic recognition elements in biosensors or the imaging of biological systems. Many of these systems show a pronounced dependence on the temperature due to changes in reaction rates and changes in mass transport effects. If these are not considered, a loss of comparability between different studies may occur. In severe cases it may even reduce the significance of an investigation, if it is done at a temperature far away from the conditions the sample is usually used in. Especially biological systems are usually optimized for working in a narrow range of temperatures around physiological conditions, and during the characterisation of new catalysts it seems to be advantageous to do this in similar conditions as they are used in later.

Despite this, there are very few publications which deal with SECM experiments at non-standard temperatures or which specifically apply a certain temperature. Most studies involving SECM neglect the temperature, although SECM continuously develops toward a matured method of surface characterisation.

In the view of this deficit and for gaining additional knowledge about interfacial processes, an extension of the possible conditions during SECM experiments include the control of the temperature as an adjustable parameter. Here, we described the system setup and its specific features of a newly developed SECM instrument capable of specifically adjusting and monitoring the temperature of the sample during the experiment within the range defined by aqueous electrolytes at standard pressure. Moreover, the compatibility of complex techniques to image samples like the redox-competition (RC) mode with temperature control was established. Besides some particularities of performing SECM experiments at non-standard temperatures, first applications to investigate biological and technical catalysts (enzymes, Pt- and RhS-based catalysts) and the advantages of using the RC mode at different temperatures will be discussed.

SCANNING ELECTROCHEMICAL MICROSCOPY APPLICATIONS IN MATERIALS CHEMISTRY, BIOCHEMISTRY AND NANOCHEMISTRY

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The tremendous number of applications of Scanning Electrochemical Microscopy¹ has roots both in the great versatility and investigative potential of this technique and in the scientific curiosity and skills of those that uses it. Given these premises it is easy to understand the ever increasing number of different topics that are ground for SECM investigations and characterization.^{1, 2} This communication deals with applications of SECM in the study of new materials.

In particular results on the study of a new graphite-like porous material, currently used for bone implants, will show its potential applications both in oxygen reduction catalysis and as a suitable substrate for combinatorial electrochemistry. Another topic of investigation presented in this work embraces nanomaterials: in particular quantum dots and graphene. These materials have a great potential in energy storage and conversion, bioanalytical devices and nanotechnology in general. Results on SECM of quantum dots³ and graphene in different media and for different experiments will be given.

¹ P. Sun, F. O. Laforge, M. V. Mirkin, *Phys. Chem. Chem. Phys.*, **2007**, *9*, **802**

² M. Carano, N. Lion, H. H. Girault, *J. Electroanal. Chem.* **2007**, *599*, **349**; M. Carano, K. B. Holt, A. J. Bard, *Anal. Chem.* **2003**, *75*, **507**; Carano, M; Bond, AM, *Australian. Journal. of Chemistry.*, **2007**, *60*, **29**

³ B.Gadonne, I. Yildiz, M. Amelia, Flavio Ciesa, A. Secchi, A. Arduini, A.Credi, F. M. Raymo *J. Mater. Chem.*, **2008**, *18*, 2022–2027

Concerted Proton-Electron Transfer in the Electrochemical Oxidation of Phenols ?

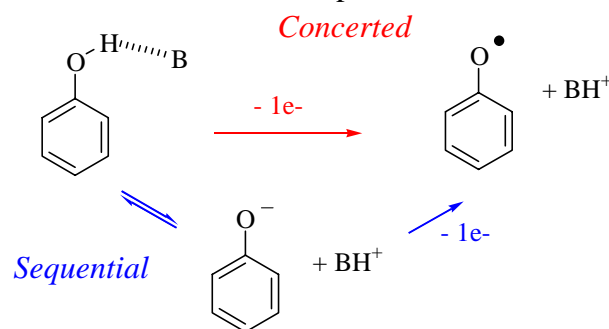
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Proton-coupled electron transfer reactions play a critical role on a wide range of natural, catalytic and artificial processes.¹ An important example is photosystem II (PSII), which converts water into oxygen and protons thanks to the light energy. A key step of the charge separation involves oxidation of a tyrosine by chlorophyll P₆₈₀⁺: both electron and proton are transferred. One may wonder if the high efficiency of this process is related to the possibility that the electron and proton transfer steps are concerted (one single transition state). Activation of water in the catalytic center of PSII by a manganese cluster also involves proton-coupled electron transfer reactions (PCET).

It thus appears that the understanding of PCET reactions at a molecular level is an important step towards deciphering the mechanism of water oxidation. It is also a necessary requirement for the future conception of artificial nanostructured biomimetic devices that would convert and store solar energy under the form of protons and electrons, i.e. hydrogen.

Focusing on tyrosine, its oxidation is a crucial step in PSII but also in many enzymatic and catalytic processes. The oxidation of mimetic phenols may follow two types of mechanism: a mechanism in which the two reactions occur in a stepwise manner and a mechanism in which proton and electron occur in a concerted manner (see scheme). The electrochemical oxidation of 2,4,6-tri-*tert*-butylphenol and phenol itself in aqueous media are good illustrative examples.^{2,3} Competition between the different pathways and possible occurrence of concerted reactions as a function of pH will be investigated and discussed using cyclic voltametry responses.



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Is Marcus Theory applicable to Electron Transfer Reactions in Ionic Liquids ?

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Marcus Theory of electron transfer (et) reactions is now well established for both, homogeneous reactions in solution and heterogeneous electrochemical reactions at electrode surfaces (1).

All the theoretical predictions of the theory, like the unexpected “Marcus Inverted Region”, the predicted solvent dependence and solvent dynamics as well as the inner-sphere contributions caused by the changes of bond lengths and bond angles are found by numerous investigations (2).

Especially the solvent dependence is a focus of ongoing investigations, since frictional solvent dynamics can dominate the rate constants, according to the diabatic or adiabatic reaction behaviour. For homogeneous intermolecular electron-self exchange reactions the solvent dependence is given by the Pekar factor $\gamma=(1/n^2-1/\epsilon_s)$, or is influenced by the solvent longitudinal relaxation time τ_L (3). n denotes the refractive index and ϵ_s is the static dielectric constant of the solvent. The solvent dependence arises from the outer-sphere reorganization energy λ_o , which is part of the activation energy ΔG^* . λ_o is a linear function of γ . This finally leads to simple relation between the rate constant k_{et} of the electron transfer and the Pekar factor γ : $\ln k_{et}$ becomes a linear function of γ . For adiabatic et-reactions the solvent relaxation time τ_L appears in the preexponential factor of the rate expression.

Such solvent dependences are found for various organic redox couples, like methylviologenes, quinones, p-phenylenediamines, cyanobenzenes, TEMPOs, cyclooctatetraene, etc.(4).

The situation completely changes if the same electron transfer reactions are measured in ionic liquids. We report on the homogeneous electron self-exchange reaction of methylviologenes (5), also on the heterogeneous electrochemical reactions of methylviologene, various quinones, p-phenylenediamines etc, in ionic liquids of different viscosities. Preliminary results are:

- 1.) No ion pairing effects are observed by ESR-spectroscopy between the radical ions and the charged ionic liquids. The ESR-coupling constants are nearly the same as in common organic solvents.
- 2.) Measured activation energies for both homogeneous and heterogeneous et-reactions are in the same range compared with activation energies in organic solvents. But the Marcus reorganization concept based on polarization effects can not be applied to ionic liquids. What is the influence of the different ionic liquids on the rate constant?

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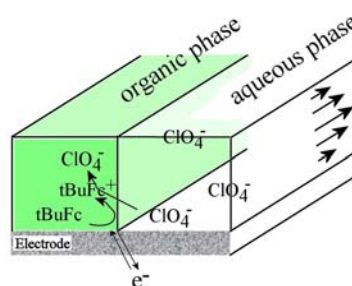
Electrochemical Processes at Flowing Liquid | Liquid | Electrode Interfaces

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A microfluidic double channel device^{1,2} (see Figure) was employed to study reactions at a flowing liquid | liquid interface in contact with a gold electrode. The rectangular flow cell was calibrated for both single phase liquid flow and biphasic liquid | liquid flow for the case of the immiscible N-octyl-2-pyrrolidone (NOP) | aqueous electrolyte system. The influence of flow direction and speed and liquid viscosity on the position of the phase boundary was examined.

The $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox system was employed in aqueous solution to calibrate the flow cell in the absence and in the presence of the organic NOP phase. A significant “undercutting” of the organic phase into the aqueous phase was observed in particular for shorter gold band electrodes. The triple phase boundary reaction zone was visualized with a



colour reaction based on the oxidation of N-benzylaniline. An approximate expression can be given to predict the mass transport controlled limiting currents even under two-phase flow conditions. Next, n-butylferrocene in NOP (without intentionally added electrolyte) was employed as the organic redox system with 0.1 M NaClO_4 as the adjacent aqueous electrolyte phase. Under these conditions the electrochemical reaction only proceeded at the organic liquid | aqueous liquid | solid electrode triple phase boundary reaction zone and significant currents were observed. In contrast to processes at conventional liquid | electrode interfaces, these currents decreased with increasing flow rate. The level of conversion at the triple phase boundary reaction zone can be further enhanced (i) at sufficiently slow flow rates and (ii) at larger electrodes. Bulk electrosynthetic processes are feasible but the reactor design has to be further improved.

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Driven motion of the third phase on the oil | water interface by three-phase boundary reactions

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A highly competitive system is the reaction at the three-phase boundary at which the electrode was exposed to both the oil and the water phase, explored by Scholz and coworkers¹⁻³. It is composed of an oil droplet mounted on the electrode in an aqueous solution. A typical cell apparatus is composed of the oil droplet including only a redox species, which is located on an electrode in an aqueous solution including supporting electrolyte⁴⁻⁷, as is shown in Fig.1A. An air bubble mounted on an oil | water interface is a probe not only of interfacial tension but also of properties of three-phase boundary reactions⁸.

This report is devoted to investigating the static and dynamic behavior of the air bubble on the O|W interface in the context of the three-phase boundary reaction of ferrocene. The bubble kept spontaneously moving on the oil|water interface without applying any force, when it is less than 0.3 mm in diameter. The motion was irregular without decay, suggesting a contribution of Brownian motion. When the three-phase boundary reaction occurred, the bubble motion stopped. It was observed only in the potential domain at which ferrocene is oxidized. The force balance of the air bubble at the O|W interface will be formulated in terms of the interfacial tensions and the buoyancy. It will be demonstrated that the electrode reaction varies the surface tension at the O|W interface to cause surface convection.

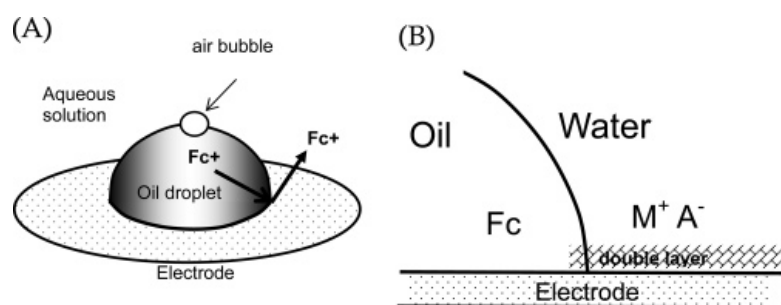


Fig.1.

Illustration (A) of a hemispherical oil droplet including an air bubble mounted on an electrode in aqueous solution, and interpretation (B) for the three-phase boundary reaction of ferrocene (Fc) in the oil phase. Supporting ions, M^+ and A^- , form a double layer.

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Electroreduction of fullerene C₆₀ coupled to ion transfer across liquid-liquid interface

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C₆₀ molecule is capable to accept up to six electrons due to triple degeneracy of its lowest unoccupied molecular orbital. Each of the reduction steps can be detected electrochemically in organic solvent.¹ The corresponding redox potentials are influenced by the solvent donicity as well as by the size of supporting electrolyte cation.²

In this work fullerene C₆₀ has been used as a redox probe to study multistep electroreduction coupled to the ion transfer across water - 1,2-dichlorobenzene interface. In our experiment a small amount of fullerene solution in organic solvent was deposited on the basal plane pyrolytic graphite electrode. The electrode was then immersed into deaerated aqueous electrolyte solution and cyclic and differential pulse voltammetry were performed.

Typically, the driving force of ion transfer is the charge difference between two immiscible phases that share an interface.³ Herein, an excess of negative charge within organic phase is generated by electrode reaction of the fullerene. In order to maintain electroneutrality within organic phase ion transfer across liquid|liquid interface has to occur.

Three sets of reduction-oxidation peaks are observed on the cyclic voltammograms and the subsequent peaks can be assigned to the subsequent one-electron transfer steps of fullerene species.⁴ Voltammogram corresponding to C₆₀ / C₆₀⁻ redox couple is stable upon cycling, indicating that charge compensation in the organic phase involves ion transfer reactions. The redox potential is strongly affected by the concentration of aqueous electrolyte and the nature of anion present initially in the aqueous solution. The nature of those dependences indicates that electroreduction of C₆₀ is followed by expulsion of supporting electrolyte anion. The effect of electrolyte on the second electroreduction step of C₆₀ is similar. The redox potential of C₆₀⁻/C₆₀²⁻ couple is also anion-sensitive and depends on aqueous electrolyte concentration. Such a behavior may be explained by interfacial ion-exchange or salt partitioning processes which results in aqueous anion extraction to the organic phase prior to electrochemical measurement.

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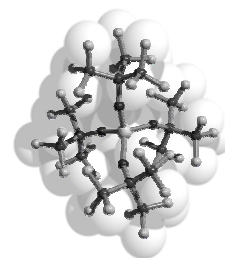
Performance of $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ salts as electrolytes.

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Weakly coordinating anions (WCAs) are a topic of current interest for academia and applied research.¹⁾ Owing to their potential to stabilize reactive and fundamentally important cations such as a free silylium ion, weakly bound Lewis acid base adducts, small carbenium ions etc. as well as to provide access to new active cationic transition metal catalysts, good supporting electrolytes as well as electrolytes for Li ion batteries much recent research was directed to the preparation of new WCAs with the goal of preparing the least coordinating and chemically most robust WCA at the cheapest price.

In this global competition for the best WCAs, the poly- and perfluorinated alkoxyaluminates $[\text{Al}(\text{OR}^{\text{F}})_4]^-$ are a recent addition.^{2,3)} We showed by a series of papers that i) these aluminates are very weakly coordinating so that the silver ion of $\text{Ag}^+[\text{Al}(\text{OR}^{\text{F}})_4]^-$ coordinates unusual ligands such as P_4 , S_8 , P_4S_3 or C_2H_4 and ii) these aluminates are also chemically very robust so that solutions of the simple Cl_3^+ cation are stable at ambient temperature for days.⁴⁾ Probably the best WCA of this series is $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$, the superposition of ball and stick and space filling model is shown on the right:



The lecture will focus on recent results on the performance of these anions as supporting or primary electrolytes.

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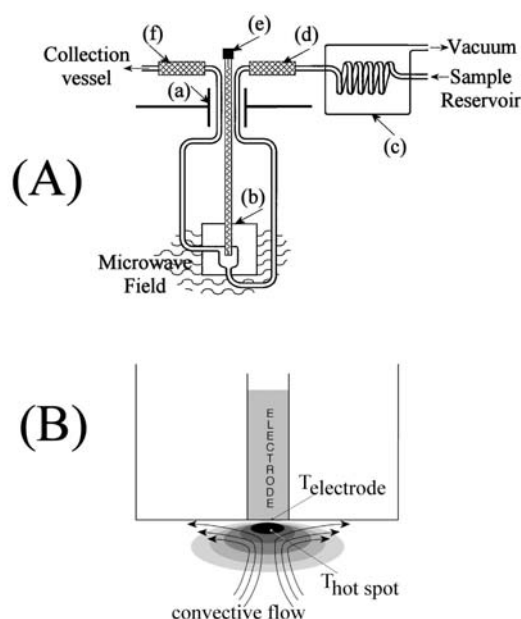
Electrochemical Processes in the Presence of Microwaves

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In situ microwave activation of electrochemical processes can be achieved at electrodes placed directly into a microwave cavity^{1,2} (see Figure). Effects of microwave radiation on electrode processes have been reported for a wide range of solvent systems (aqueous, DMSO, acetonitrile, DMF, formamide, BMIM⁺PF₆⁻) and currently new types of electrodes for improved electroanalytical processes are under development. Three orders of magnitude current increases and considerable temperature enhancements are observed and explained based on the interaction of microwave radiation with the liquid dielectric (electrolyte). Electrochemical processes under superheating or “hydrothermal” conditions (up to 480 K at ambient pressure) are observed when glycerol is employed as an additive.



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Ironoxide-polypyrrole-nanocomposites synthesized by a core-shell route

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In this presentation we describe the synthesis of a core-shell nanocomposite (Fe@CPB-PPy) based on iron-cores (Fe) and cetylpyridinium-polypyrrole-shells (CPB-PPy) and the dissolution of Fe-cores to receive porous CPB-PPy-shells. The particles were characterized by SEM, EDX, XRD, TEM, FTIR, BET and electrochemical methods.

The synthesis of iron particles was performed by reduction of FeSO₄ with boron hydride in alkaline solution. The coating of the Fe-cores was realized according to a process by Hyun et al.^[1]. In a first step CPB was used to achieve a Fe-CPB-micelles suspension. In a second step pyrrole was added into the micelles-suspension. Polymerization was accomplished by chemical oxidation with Fe₂(SO₄)₃. The dissolution of Fe-cores was carried out chemically in diluted hydrochloric acid or electrochemically.

SEM and TEM micrographs of Fe@CPB-PPy show particle sizes smaller than 50nm with a wide range of size distribution. From BET analyses an average surface area of about 20m²/g was determined.. Furthermore TEM image in figure 1 shows that many Fe@CPB-PPy particles contain more than one Fe-core (dark spots). TEM image in figure 2 shows CPB-PPy particles after core dissolution.

An increase in surface or porosity after Fe-core dissolution can be expected. Further investigations are in progress.

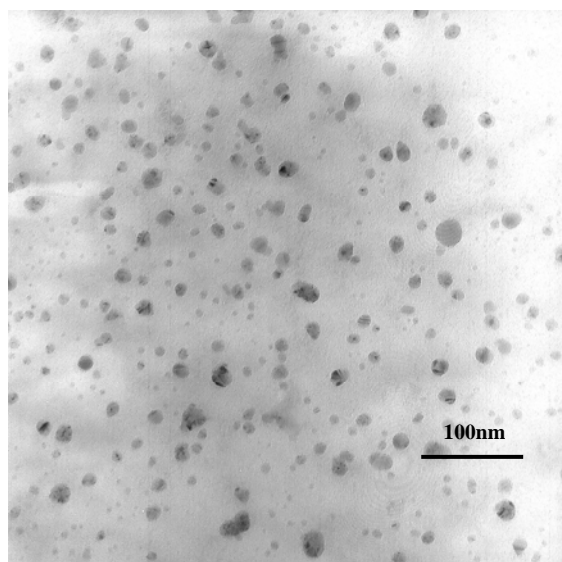


Figure 1: TEM-image of Fe@CPB-PPy particles

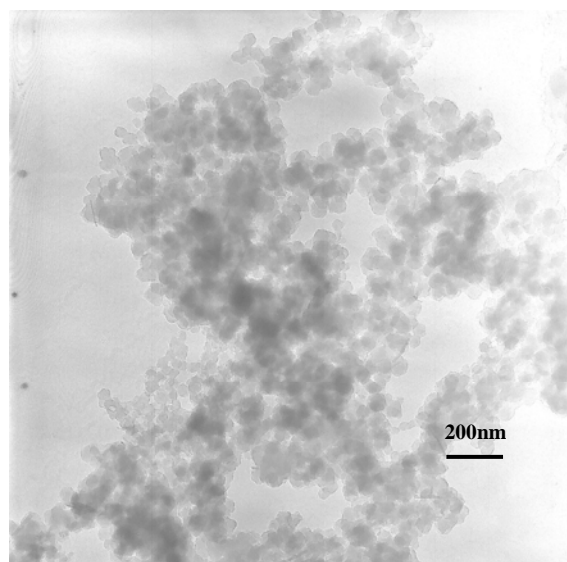


Figure 2: TEM-image of CPB-PPy particles after dissolution of Fe-cores

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Preparation of 110 Faceted Single Crystalline Au Nanostructures and their Electrochemical Properties

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Directional solid state decomposition of eutectoid alloys is a novel method for the preparation of nanoparticles. The entirely different preparation route gives access to uncommon structures. This route is unique since the less stable 110 surface dominates which typically never forms in nanoparticles. It is of particular interest to study the 110 faceted gold nanostructures ranging from small platelets to high aspect ratio nanobelts. Details of the preparation process, a thorough characterisation and examples of their electrocatalytic properties will be given.

The preparation is a solid state reaction; the so-called eutectoid decomposition being performed in a Bridgman furnace [1]. This allows for a unidirectional heat extraction that directs the decomposing alloy into a self organised structure consisting of an iron single crystal with embedded gold nanoplates or nanobelts. The surface of this ensemble can be electrochemically treated to release a desired fraction and length of the gold nanobelts [2]. Alternatively a complete dissolution of the iron matrix is possible that yields macroscopic amounts of gold nanoplates or nanobelts.

The structure is characterised by HRSEM and HRTEM providing a detailed view into the microstructure of the gold nanobelts and nanoplates. The nanoplates are 20-30 nm thick and 100 nm in square. The nanobelts are 20-30 nm thick, 200-300 nm wide and more than 20 μm in length, resulting in an extreme aspect ratio of more than 1000! Both structures are single crystalline and iso-oriented as confirmed by HRSEM, HRTEM, SAED and EBSD [3]. The unique properties of these gold nanoparticles directly result from the preparation that yields preferentially the less common (110) surface [4]. This is the starting point for both, physical and electrochemical applications.

The electrochemical characterisation is a key to the surface properties of this new class of materials. UPD deposition of lead and its catalytic properties for oxidation reactions do not only confirm the gold (110) surface but also opens the possibility to study its catalytic properties in comparison to preferential (111) surface gold structures for various reactions such as methanol oxidation and glucose oxidation. These results are compared to chemically synthesised gold (111) particles demonstrating the dominant influence of the crystallographic facet [5].

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Vertically aligned carbon nanotube electrodes prepared by thermal chemical vapor deposition and by chemical assembly on carbon substrates

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Vertically aligned carbon nanotubes (VACNTs) and carbon nanofibers (VACNFs) are excellent candidates for the fabrication of carbon-based electrodes. Multiwalled CNTs (MWCNTs) and CNFs have metallic conductivity and when vertically aligned with open ends, fast rates of electron transfer with redox species are obtained.¹ Furthermore, the relatively high density of terminating carboxylate groups at the open tube ends provides convenient routes for immobilizing species of interest.²

A straightforward procedure is described for preparation of arrays of macro- and microdisk electrodes comprising bundles of vertically aligned carbon nanotubes (VACNTs).^{3,4} Arrays are fabricated by thermal chemical vapor deposition (CVD) synthesis directly on a planar carbon film support (Figure 1). Use of standard micro- and nanolithography procedures for patterning the bilayer catalyst spots enables arrays to be grown with controlled electrode diameters and spacings. After insulating the arrays with SU-8 epoxy and exposing the VACNT tips by polishing or treating with O₂ plasma, the electrodes are robust and re-usable.

In a second approach to VACNT electrodes, we have chemically assembled single-walled CNTs on tether layers covalently grafted to carbon surfaces. The electrochemical responses of redox probes have been compared at VACNT electrodes prepared by CVD and by chemical assembly, and at randomly oriented CNT mats.

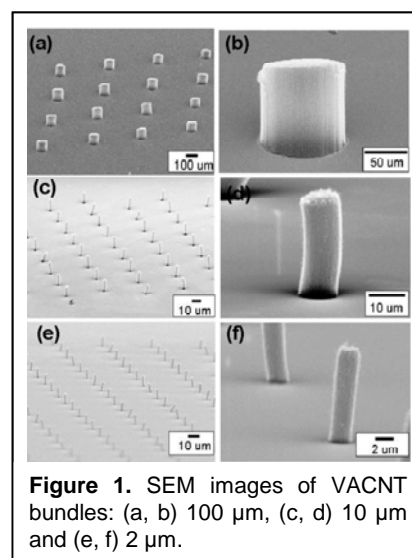


Figure 1. SEM images of VACNT bundles: (a, b) 100 μm, (c, d) 10 μm and (e, f) 2 μm.

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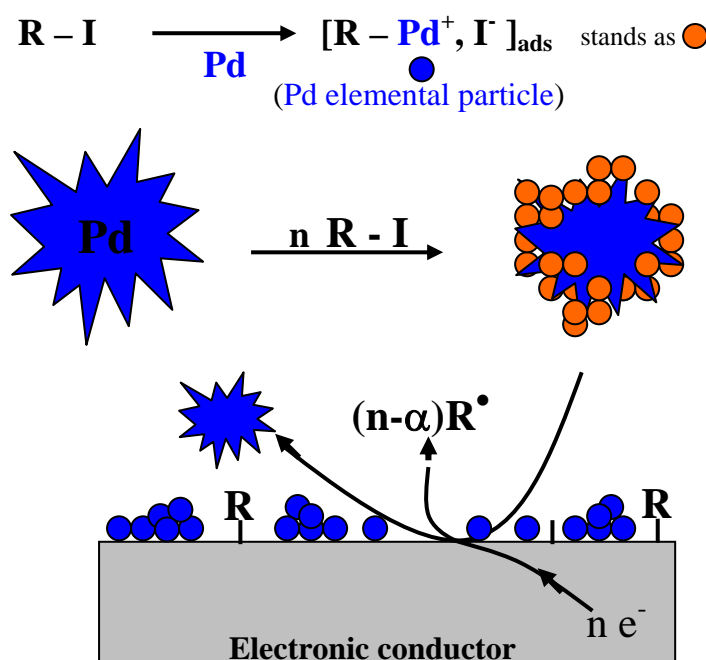
Alkyl halides as vectors for the facile coverage of electrified conductors by palladium, silver, gold, and platinum nano-particles.

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The easy reaction of primary alkyl halides **RX** (**X = Br or I**) with palladium metal is used to transport elemental palladium onto solid cathodes (Glassy carbon, gold, platinum, nickel, etc...). The principle is to create suspensions of palladium particles in solutions of **RXs** in weakly protic polar solvents. The reaction is particularly effective with **RIs** and then electroactive species are **[R-Pd⁺, I⁻]** that cover palladium grains and may discharge (according to a one-electron process to lead to homo-dimers quasi-selectively [1]) at electrified substrates for liberating **Pd⁰** (displayed in Scheme 1) This procedure efficiently [2] produces palladium nano-aggregates and easily yields chemically modified surfaces with a large palette of substrates.

Recent investigations using other vectors more efficient [3-4] allow now the deposit of almost **all** transitions metals (Au, Pd, Pt, Ag, Ni, Cu, etc...) nanoparticles onto many electrified conducting et semi-conducting (at their n-doped state) materials under very simple and inexpensive ways.



Scheme 1

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Main Strategies to Direct Localized Organic Grafting on Conducting and Semiconducting Substrates

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Electrochemistry offers a certain number of assets to localize at a micronic or sub-micronic scale, organic thin layers covalently bound to metallic or semiconducting substrates. The present contribution will focus on several strategies developed in order to direct a covalently grafted organic coating on a localized level on conducting or semiconducting substrates. Electrografting is achieved by the electrochemical reduction of suited precursors on substrates, which leads to a strongly grafted film. Our group has historically been developing the electrografting of vinylic polymers via an electro-induced anionic polymerization that starts from a precursor chemically bound to the electrode.¹ A second family of precursors, aryl diazonium derivatives, has also been investigated.^{2,3} As the grafting is electro-induced and originates from the surface, it is strongly dependent on the local efficiency of the electron transfer to the electro-active species in solution. For composite substrates, that efficiency is triggered by the local composition of the surface and the selectivity depends obviously on the difference between the work functions of the composite materials. For homogeneous substrates, the efficiency of the local electron transfer may be driven by photo-induced or field-induced means, allowing the patterning of a homogeneous conductive substrate with a lateral resolution depending on the size of the mask in the first case and the shape of the tip in the second one. With the el-AFM tool, a nanometric resolution is likely to be reached.

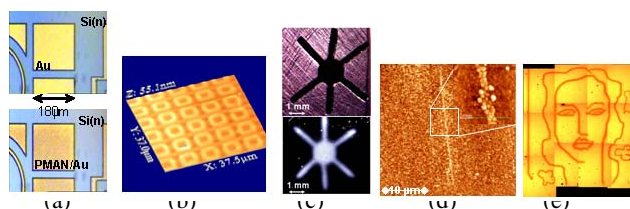


Figure : (a) optical image of a Au/Si composite substrate before and after electrografting process⁴, (b) AFM image of a locally doped silicon substrate after electrografting process^{5,6} (c) photo-induced printed image of the mask on a photosensitive substrate⁷, (d-e) line and complex design printed on a gold substrate by el-AFM and SCEM technologies respectively^{8,9}.

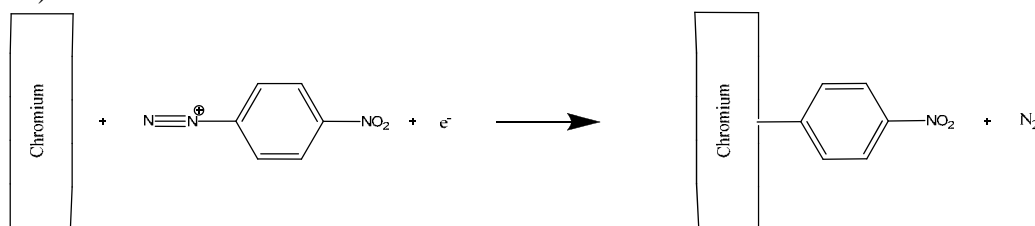
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Electrochemical Grafting of p-Nitrobenzenediazonium Tetrafluoroborate on Chromium

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The ability to modifying specific physical and chemical properties of surfaces has a large potential for many industrial processes. This can be obtained by electrochemical grafting of aryl diazonium salts onto various metal surfaces. Despite this potential in surface modification of metal surfaces very few investigations of grafting aryl diazonium salts onto stainless steel have been carried out (1). Stainless steel is a ferric alloy containing nickel and chromium that pacifies the surface towards corrosion. This passivation mainly stems from the coverage of the surface with a thin layer of chromium oxide. Hence grafting onto stainless steel is influenced by the alloying metals chromium and nickel, and an investigation of their grafting abilities is therefore pertinent. Nickel and iron have previously been electrochemically grafted with aryl diazonium salts (2, 3) but to our knowledge no data have been published on grafting of aryl diazonium salts onto chromium. Our work shows that it is possible to electrochemically graft p-nitrobenzenediazonium tetrafluoroborate onto chromium surfaces (scheme 1).



Scheme 1

Electrodes (coated microscope glass slide and metal rods) of chromium and nickel (for comparative reasons) were applied in this investigation of the grafting process. The grafted chromium surfaces were analysed by cyclic voltametry (CV), polarization modulated infrared reflection absorption spectroscopy (PMIRRAS) and X-ray photoelectron spectroscopy (XPS).

CV results showed a clear reduction peak and blocking effects corresponding to the reduction of the diazonium group. After cleaning of the grafted surfaces by sonication for 5 min in acetone results from both CV, PMIRRAS and XPS showed the presence of the nitro group on the surface.

In conclusion it was shown that it is possible to electrochemically graft p-nitro-diazonium tetrafluoroborate onto chromium surfaces. Future research will be conducted in investigating the electrochemical grafting of stainless steel with aryl diazonium salts.

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ELECTROCHEMILUMINESCENCE BEAD-BASED MICROARRAY FOR MULTIPLEXED SANDWICH IMMUNOASSAYS

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New techniques to realize multiple analyses simultaneously are eagerly needed and being developed. For example, fluorescence is widely used to image sensor microarrays and allows for the detection of a large number of analytes simultaneously [1]. As an alternative, electrochemiluminescence (ECL) is a very sensitive readout mechanism and has already been commercialized [2]. Here we present a new class of sensing microarray that combines ECL detection and the ability to image multiple analytes in a single sample.

The biochip consists of encoded beads modified with antibodies, deposited by solvent evaporation in the wells of a microstructured electrode (Fig. 1 A, B). This electrode is an optical fiber bundle containing 50,000 optical cores that have been etched and then gold-coated.[3] The randomly ordered microarray is incubated with the sample antigen and then with the biotinylated detection antibody (Ab). The ECL label, ruthenium (II) trisbipyridine (Ru complex), is introduced by dipping the array in a solution of streptavidin (SA) modified with a Ru complex (Fig. 1C). The luminescence is generated during a cyclic voltammogram, using the microarray as the working electrode in a buffer containing tri-n-propylamine (coreactant). ECL is collected through a microscope with an electron-multiplying CCD (EM-CCD) camera and the signal from individual beads is imaged.

This bead-based platform for performing immunoassays by imaging the ECL enables us to detect multiple analytes simultaneously. For example, using an array with three kinds of beads, each of them modified with different antibodies, we were able to detect samples containing combinations of the corresponding antigens. Some cross reactivity experiments were also run and showed good specificity of the sensors. This work demonstrates for the first time to our knowledge, the possibility of imaging individual sensing microbeads by ECL and to realize multiplexed sandwich immunoassays.

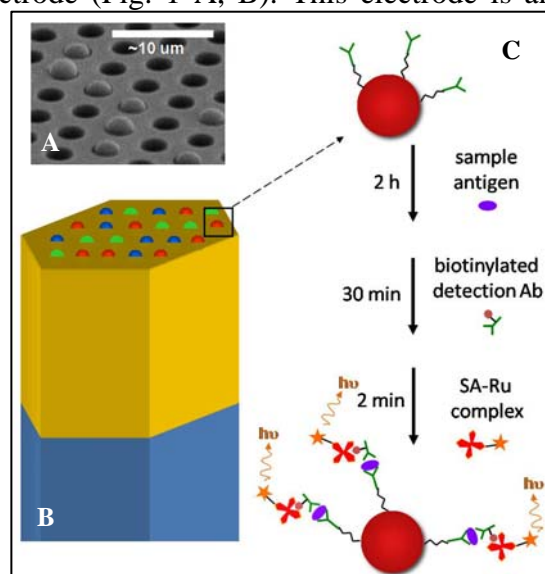


Figure 1: A) SEM image of the beads in the etched fiber bundle; B) Scheme of the randomly ordered microarray; C) Schematic sandwich immunoassays with the ECL label.

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Synthesis and electrochemical modulation of the actuator properties of a polypyrrole directed phenazine derivative for implementation as a molecular hinge

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An actuator is a device which promotes mechanical work under the application of an external stimulus (Vidal F et al., 2006). Conjugated conducting (CP) polymers are a viable and interesting alternative as actuators, since they work with low potentials and they experience volume changes that are associated with conformational changes in their structure (Hara S et al., 2004; Otero TF, 1997). Phenazine 2,3- diimino (pyrrole -2- yl) was synthesized by the condensation reaction with a yield of 61%. The product was then doped with 1,2-naphthaquinone-4-sulfonica acid, which is known to improved the electrochemical activity and processability of polypyrrole. The chemically synthesized product was characterized by FTIR, NMR and SEM analysis to confirm whether the desired product was obtained.

Subsequently, electrochemical polymerization of phenazine 2, 3- diimino (pyrrole -2- yl) was carried out HCl/DMF solution at a glassy carbon electrode. The thin film produced was characterized by cyclic voltammetry at different scan rates in 0.1M HCl to evaluate the kinetic parameters. Electrochemical impedance spectroscopy (EIS) measurements were then performed in 0.1M HCl, NaCl, KCl and CaCl₂, to evaluate the volume changes that occur during reduction. Evaluation of low frequency impedance within the potential range 100 – 500 mV at 100 mV intervals revealed that the formal potential could be determined as 300 mV. The trend in the volume change was observed to be in the order CaCl₂ > KCl > NaCl > HCl, which corresponds to the size of the cation i.e. an increase in the size of the cation produced an increase in the low frequency impedance which was interpreted as the volume change upon reduction. Equivalent circuit modeling of the interfacial parameters modeling the volume change will be presented.

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New transition metal containing electroactive polymer materials as catalysts for oxidative functionalization of organic substrates and C-C bond formation

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A development of sustainable science and technology demands powerful catalysts with tunable multifunction. The polymer backbone with easily tunable physical and chemical properties provides a convenient background for the design and creation of multifunctional molecules.

A series of new redox-active polymers with tunable conformational lability, capable of coordination to transition metal moieties (Cu(I), Pd(II), Ni(II), etc.) were used in electrosynthesis with various types of sacrificial anodes to obtain the corresponding metal-containing polymers. Thus obtained polymer systems were investigated as catalysts for electrocatalytic processes of various types, as dependent on the nature of the catalytic center: aerobic oxidation of aliphatic alcohols and amines to carbonyl derivatives, cross-coupling reactions of various types and some others and demonstrated excellent efficiency. The voltammetric investigation of metal-polymers revealed a significant role of conformational properties of polymer ligand in stabilization of coordinatively unsaturated metal units, which are catalytically active, thus allowing an express electrochemical diagnostics of an optimal catalytic system.

The mechanism of electrocatalytic aerobic oxidation of organic substrates was elucidated from the electrochemical, spectral and DFT data. It revealed some similarities with copper enzymes mediated oxidative reactions occurring in nature. The possibility of the obtained redox-active macromolecules to mimic the active site of certain copper containing enzymes capable of reversible binding and activation of dioxygen will be discussed. The replacement of a protein part of enzyme, which is very sensitive to external influences, with a stable polymer matrix capable of reserving an optimal coordination environment of metal centers, seems to be rather promising. These processes investigated are of general interest in electrocatalysis and in the bioinorganic chemistry of copper.

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Elaboration of porous bismuth film electrodes and their application in electroanalysis

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Bismuth film electrodes (BFEs) have been recently suggested for electrochemical stripping analysis as an alternative to mercury electrodes due to the much more environmentally friendly bismuth¹. The advantageous analytical properties of BFEs in voltammetric analysis are attributed to the property of bismuth to form fused alloys with heavy metals, which is analogous to the amalgams that are formed by mercury².

Metal electrodes with an ordered pore structure have the obvious advantage of a very high active surface area, which can lead to currents up to two orders of magnitude higher than those of classic flat electrodes. One straightforward application of such electrodes is in the field of electrochemical sensors and biosensors³⁻⁶.

This work deals with the elaboration of porous bismuth film electrodes in order to obtain sensitive tools for trace analysis (environmental, clinical and food analysis) because these electrodes show an increase in electrochemical performance due to the porosity that gives these materials a high active surface area. The porous bismuth film electrodes in this work

were prepared by electrodeposition of bismuth through a colloidal crystal template followed by dissolution of the template. Self-assembled layers of polystyrene latex particles were formed by slow evaporation of water from the latex suspension⁷. After electrodeposition of bismuth the polystyrene spheres are fully removed by washing in toluene to leave an interconnected network of pores within the metal film, the size of which is determined by the polystyrene spheres used to prepare the template. These electrodes were successfully tested by stripping voltammetry and show significantly improved detection limits.

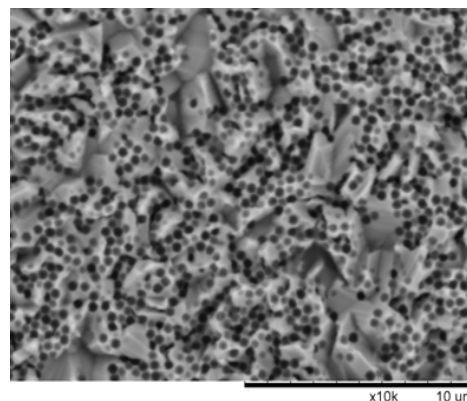


Fig.1: SEM of porous bismuth film.

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Surface Functionalization via diazonium salt electrochemical reduction : application to chemical sensor

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Interest in surface modification and derivatization is growing in the fields of material science, catalysis, chemical and biological sensing, molecular electronic, corrosion protection... The electrochemical reduction of aryldiazonium salts led to the synthesis of thin layers (thickness in the nanometer range) bearing a wide range of functional groups on to a large variety of conductive substrates such as carbon, Pt, Au, Si, Fe, Zn¹⁻²...

Recently surface grafting via electrochemical reduction of aryldiazonium salt has been mentioned for various applications in numerous papers. Thus a complete understanding and control of the deposition and the structure of these layers is required for their successful applications. The purpose of this work is to examine and to control the structure of the organic layer grafted on various electrodes via electrochemical reduction of 4-nitrobenzene diazonium salt. The characterization of the grafted layer is investigated with the use of cyclic voltametry, the infrared reflectance absorption spectroscopy and the X-ray photoelectron spectroscopy. The growth of the layer is tracked in situ by quartz micobalance³ and ex situ by atomic force microscopy. The grafting of the aryl layer is achieved via chronoamperometry or cyclic voltametry.

A new application as on site trace element sensor will be presented and will show the interest of screen-printed electrode⁴ grafted via diazonium salt for environmental analysis. Electrochemical grafting was preferred to control both properties and structure of the grafted layer. Electrodes properties, performances and reliability were then investigated for on site measurements. Grafted screen-printed electrodes were finally successfully used for copper and uranium at sub $\mu\text{g L}^{-1}$ level in natural water samples. These novel and easy to realize grafted screen-printed electrodes appear as one of the most promise tool for fast, simple and reliable analysis on site.

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Synthesis of FeCr alloy nanoparticles by pulsed sonoelectrochemistry

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This study describes synthesis of FeCr alloy nanoparticles from solutions containing metal chlorides and glycine (1), by using a method which couples electrodeposition of metals with the employment of high power ultrasound (2).

The production of alloyed nanoparticles was performed using a 20 kHz titanium alloy horn ultrasound generator, a “sonoelectrode” generating short current pulses (t_{ON}) triggered and followed immediately by ultrasonic pulses (t_{US}) (3). The primary role of ultrasound was to induce cavitation phenomenon in the electrolyte and the ablation of the metallic nuclei from the cathodic surface (4). Nuclei formed on the titanium surface during t_{ON} were ejected into the electrolyte during t_{US} . Acoustic streaming provided the agitation of the electrolyte near the horn tip, improving the mass transport and allowing the system to work under charge transfer control (5). A rest time (t_r) restored the initial conditions close to the sonoelectrode.

The final product was a suspension of nanoparticles with high purity and high surface/volume ratio, which could be controlled by varying process parameters like time management and current density.

In this work the effect of temperature on process efficiency and nanoparticles features was investigated, and syntheses of nanopowders having different Fe/Cr ratio were carried out in order to determine the influence solution chemical composition on obtained materials.

Produced nanopowders were characterized structurally, morphologically and chemically by TEM, SEM, X-EDS, XRD and SAED.

Results showed that (i) bath's temperature affected process efficiency and best values were obtained by using low temperatures; (ii) the observed *bcc* crystalline structure was influenced by chromium content in produced nanoparticles; (iii) average grain size was ~ 10 nm; (iv) glycine content affected both process efficiency and chemical composition of nanopowders, higher amount of iron was detected in nanoparticles obtained from baths containing this organic compound; (v) nanoparticles were agglomerated in clusters and formed three-dimensional structures, called secondary particles, having mean size of ~ 200 nm.

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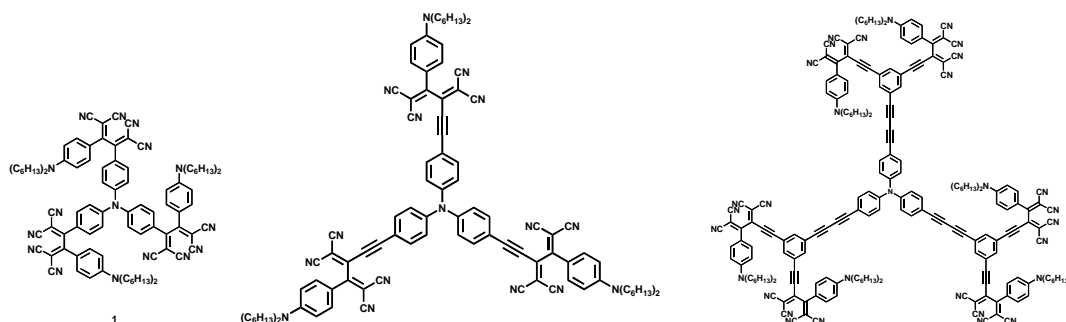
Electrochemical investigation of oligomeric donor –substituted 1,1,4,4-tetracyanobuta-1,3-dienes.

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Organic electron donor-acceptor (D-A)-substituted systems have attracted considerable interest as candidates for use in electronic and optoelectronic devices (1). A new class of potent charge transfer chromophores has been synthesized recently (2,3). A series of original oligomeric donor-substituted 1,1,4,4-tetracyanobuta-1,3-dienes (TCBDs) with an electron-donating triphenylamine core have been synthesized and their structures are shown below (4).



Their electrochemical behaviour was investigated and their redox properties are quite remarkable. Several reversible electron transfers were observed and their potential evolution are rather original. The redox behaviour clearly shows that the aniline donors substituents are oxidized at the same potential, whereas the TCBDs are reduced stepwise at different potentials indicative of more or less strong interactions between the acceptors. Their evolution will be presented and discussed.

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Thiahelicenes: molecular structure and electrochemical activity

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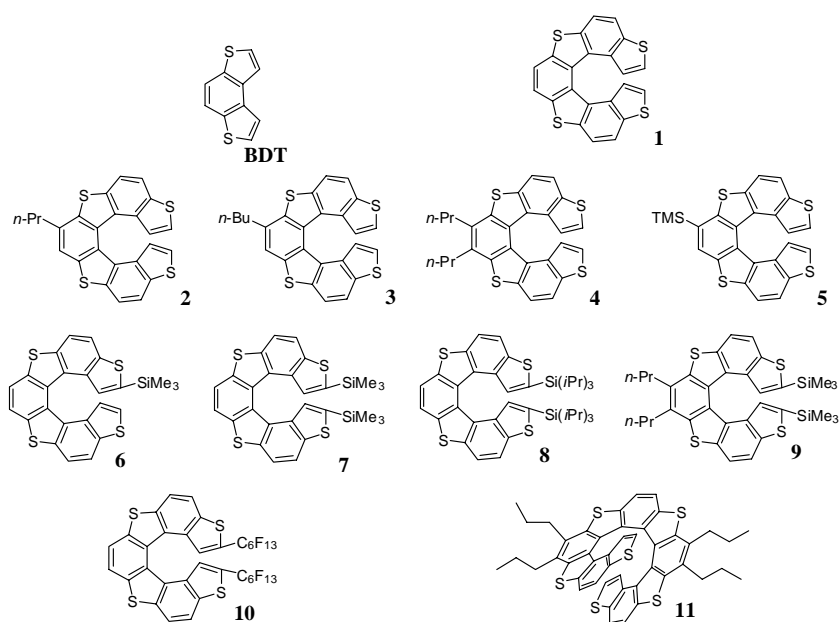
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Thiahelicenes are poly-condensed heteroaromatic molecules characterized by a chiral helix-like structure including multiple thiophene units, with a lowering effect on the oxidation potentials and a shrinking effect on the band gaps. As a consequence they can be regarded as electrochemically and



optically active conducting materials, exhibiting interesting properties under electrical or magnetic polarization, and are under study for non-linear optics (NLO) applications. The present extensive investigation on eleven thiahelicenes with different chain length and functionalization (including the first example of a thiahelicene with perfluorinated alkyl chains) together with precursor benzodithiophene provides a deep insight on the structure vs electrochemical activity relationship within this attractive compound class, focusing on both electron transfer (ET) properties and oligomerization ability (hinging on free positions on terminal thiophene groups).

Bossi, A.; Falciola, L.; Graiff, C.; Maiorana, S.; Rigamonti, C.; Tiripicchio, A.; Licandro, E.; Mussini, P.R., *submitted to Electroch. Acta* (2009)

Electrochemical characterization of electroactive polymers with potential applications in organic solar cells

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Organic solar cells represent a new type of solar cells based on composites of an electron-donor (p-type) and an electron-acceptor (n-type) material. The low consumption of material and the application of efficient production techniques offer great potential for cost-efficient production of these solar cells.

In my talk I will show results on the electrochemical characterization of redox polymers bearing triarylaminines as pendant electroactive units and on conjugated polymers, e.g. poly(3-hexyl thiophenes). Both types of polymers were synthesized in our laboratories and are currently investigated as electron donors in organic solar cells.

We use cyclic voltammetry coupled with in-situ conductance and spectroscopic measurements to study (opto-)electronic properties, in particular the potential of doping and conductivity mechanisms of these redox-active polymers.

Block copolymers consisting of the above-mentioned polymers and neutral, sacrificial polylactides were further synthesized and characterized. Block copolymers are particularly interesting because they typically self assemble into ordered microdomain morphologies with length scales of about 5-50 nm. Upon degradation of the sacrificial block after structure formation polymer films with nanopores can be obtained. Ultimately these nanoporous polymer films shall be employed as templates for the electrodeposition of electron-accepting inorganic materials.

Novel spider-like multithiophene architectures: redox properties and electrochemical polymerization

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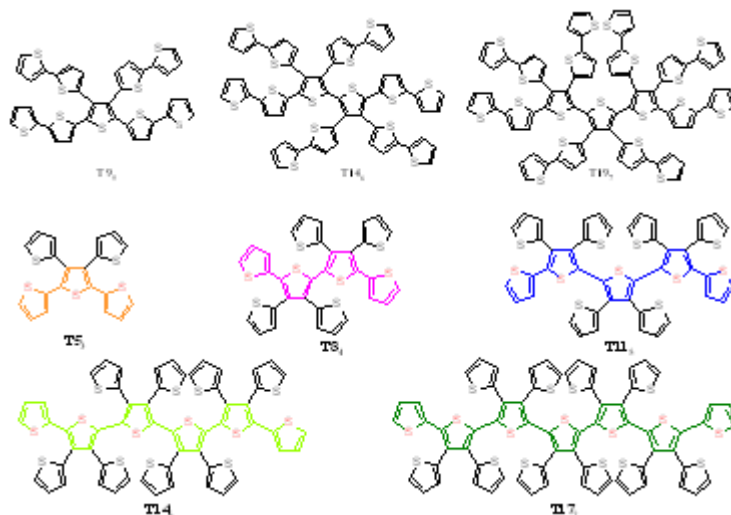
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Careful analysis and comparison of optical and electrochemical data available in recent literature for multi-thiophene molecular assemblies suggests some basic rules for the design of structurally simple and easily accessible oligothiophenes endowed with properties not far from those exhibited by much more complex and synthetically demanding architectures.

The redox properties and polymerization ability of a novel class of *spider-like*⁽¹⁾ multithiophene oligomers (right) tailored according to these indications will be discussed, particularly aiming to achieve a rationalization of the structure / property relationship. Absorption and electrochemical data are in



good agreement and point to a high π -conjugation level, comparable to that displayed by much larger assemblies. Optical and electrochemical properties of the films resulting from electrochemical polymerization, including charge trapping phenomena, will be also discussed.

The discussion will be complemented and contrasted with the case of Tn (left), a structure of peculiar geometry expressly designed to act as a 3D cross-linker for electrochemical copolymerizations in the presence of suitably functionalized comonomers, aiming to the preparation of Molecularly Imprinted Polymer (MIP) sensors.

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Electrochemical study of the pyrrole derivative 1,3,4,6-tetra-O-acetyl-2-amino-2-deoxy-2-(pyrro-1-yl)- β -D-glucopyranose (Py-GSATA)

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Using cyclic voltammetry, the pyrrole derivative Py-GSATA was electrochemically characterized. All experiments were carried out in acetonitrile containing 0.1 M tetrabutylammonium perchlorate at vitreous carbon and platinum disk electrodes. Py-GSATA showed two irreversible oxidation signals, the first at 1.24 and the second at 1.54 V vs. Fc^+/Fc . Multisweep cyclic voltammetry under different experimental conditions showed that is not possible to electropolymerize this pyrrole derivative. Surprisingly, bulk anodic electrolysis of Py-GSATA generated a single electroactive soluble product which could be reduced at -0.35 V vs. Fc^+/Fc . Mass spectroscopy of the solution revealed the generation of a dimeric species of the parent compound. ESR spectroscopy of the electrolyzed solution proved that a persistent radicalic species had been generated which was stable at least for six months at 5°C. UV-Vis spectroscopy was consistent with the existence of chain-like cation-radical oligomers. Finally, in order to propose a plausible mechanism and to explain the presence of the dimer in solution, molecular modeling using B3LYP/6-31+G** level of theory was used for analyse the stability of the electrogenerated species. The proposed mechanism involved a disproportionation reaction of the cation-radical dimer to fulfill the charge consumed during the electrolysis of the starting material.

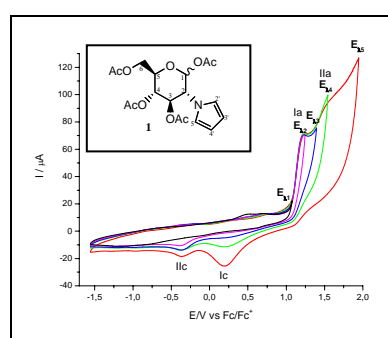


Figure 1. CV of Py-GSATA (1 mM) in ACN and TBAP 0.1 M at different inversion potential values: WE= Pt, $v=1000 \text{ mVs}^{-1}$. $E_{\lambda 1}=1.07 \text{ V}$, $E_{\lambda 2}=1.24 \text{ V}$, $E_{\lambda 3}=1.39 \text{ V}$, $E_{\lambda 4}=1.54 \text{ V}$ and $E_{\lambda 5}=1.94 \text{ V}$.

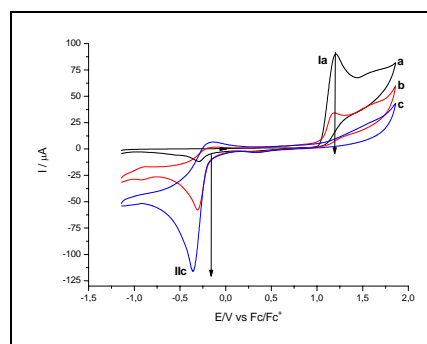


Figure 2. CV survey of the Py-GSATA (20 mM) electrolysis at 1.35 V vs. Fc/Fc^+ in ACN and TBAP 0.1M, using Pt electrodes in a divided cell: a) 0, b) 1.15, and c) 2.3 F/mol.

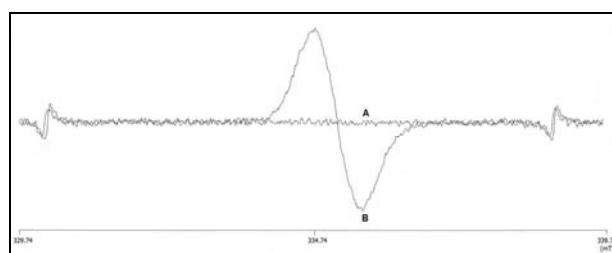


Figure 3. ESR spectra of: A) Solution containing TBAP 0.1 M in ACN and Py-GSATA 20 mM (corresponds with figure 2-a), and B) Same solution analyzed after total electrolysis at 1.35 V vs. Fc/Fc^+ (2.3 F/mol and corresponds to Figure 2-c)

**The influence of the phenazine structure
on the polaron formation in polyaniline:
An *in situ* ESR-UV-vis-NIR spectroelectrochemical study**

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It is well accepted in the scientific community, that polyaniline consists of a linear arrangement of the monomers. Since the early work of Willstätter the phenazine rings have been considered as a part of the polymer chains [1]. While most studies on the electronic structure of polyaniline and the changes upon doping use the linear structure model the influence of phenazine structures on the formation of charged states in polyaniline is not yet studied and understood in detail. Here we present the ESR-UV-vis-NIR spectroelectrochemistry of the copolymer of aniline und a phenazine derivative (3,7-diamino-5-phenylphenazinium chloride, phenosafranine) upon charging. While the structure of the copolymer has been confirmed by mass spectrometry and IR spectroscopy spectroelectrochemistry was done at polymer films prepared by electropolymerization.

It has been shown that *in situ* the ESR-UV-vis-NIR spectroelectrochemistry is a perfect tool to follow the formation of polarons in conducting polymers and copolymers. We demonstrate that the polaron formation in polyaniline and the copolymer is different from the charge injection in the homopolymer film. The increase and the maximum of the ESR signal in the copolymer and the polyaniline is delayed to the first redox peak compared to the charge transfer. The spectroelectrochemistry at the copolymer films points to a preferred stabilization of bipolarons in the formation of charged states at the beginning of the charge transfer reaction instead of polarons which are formed via symproportionation reactions [2].

Furthermore, the influence of phenazine rings on the middle peak in the cyclovoltammograms of polyaniline was studied proving that the middle peak is not associated with the presence of phenazine rings in the polymer.

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