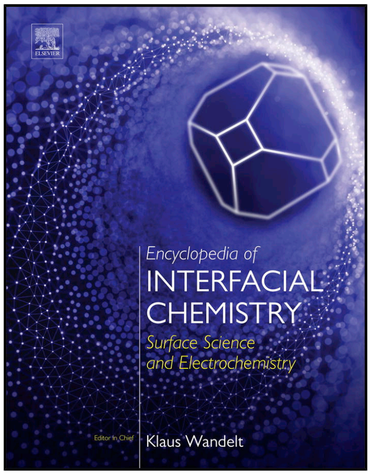

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Chemical Functionalization With Electroactive Species

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Introduction

There is great interest in the chemical modification of surfaces with organic layers because of the enormous change that the addition of even a monolayer on a surface can cause in the properties of a material. In recent years there has been an increase in interest in the modification of surfaces with organic materials towards chemical functionalities. The deposition of thin layers or monolayers of organic molecules on conductors and semiconductors is a way of giving functionality to the surfaces. This new functionality can be designed to create devices with applications such as chemical and biological sensors, microelectronics and protection against corrosion, among others.

The irreversible immobilization of electrochemically reactive molecules on different types of conducting and semiconducting electrodes, such as metals, semiconductors, carbon, and metal oxides, is one of the most important ways of chemically modifying surfaces. The attachment of these molecules onto electrode surfaces has been motivated to take advantage of their specific properties observed in a solution. An example of its application can be found in electrochemical sensors, in analytical devices in which an electrochemical device serves as a transduction element. These devices are of particular interest because of practical advantages, such as operation simplicity, low expense of fabrication, and suitability for real-time detection. Another use for this kind of surface modification is related to the continuous geometrical scaling of Si-based CMOS (complementary metal–oxide–semiconductor) transistors, which features technical difficulties, such as the lack of effective dielectric materials at nanometer scale. Hybrid transistors that incorporate organic/inorganic molecules into embedded interfaces of CMOS devices have been considered as a promising alternative. Furthermore, one of the most promising features of hybrid devices is their use in nonvolatile memory technology with potential advantages which include unique capacitance (charge–voltage) and conductance (current–voltage) characteristics owing to multiple stable redox states that are accessible in an inorganic/organic compound.

There are many procedures available for immobilizing strongly and durably such electroactive reagents and include chemisorption, self-assembly, the covalent bonding between the redox-active reagent, and either the electrode surface or a surface-bound chemically reactive unit, and electrostatic entrapment. All of these procedures result in the formation of monolayer, multilayer, or polymer films. The monolayer approach offers a wide choice of functionalities for molecular-level control of layer structure (homogeneity, ordering of organic chains) and surface chemistry. Multilayers and polymers, in spite of their usually more disordered arrangement, offer some advantages in terms of higher surface coverage, larger electrochemical currents which make, for example, more efficient electrocatalysis, higher apparent electrochemical stability, and more efficient passivating layer against corrosion phenomena.

In the next sections we shall give a brief description of some of the different available methods for surface modification with electroactive species.

Covalently Bound Electroactive Monolayers

The chemical modification of semiconductor or metallic surfaces with functional molecular groups or structures constitutes a crucial step towards future applications in numerous scientific fields. While there are many possible pathways, the covalent modification of surfaces with functionalized organic monolayers is a smart approach for designing novel well-defined interfaces for molecular electronics, photovoltaic devices, and chemical/biological sensing.

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Self-Assembly of Electroactive Thiols on Metal Surfaces

Self-assembly is the construction of systems without control from external sources other than that provided by the environment. Self-assembled monolayers (SAMs) are examples of intermolecular self-assembly that takes place at gas–liquid, gas–solid, and liquid–solid interfaces. Solid surfaces of metals, semiconductors, and oxides with different topographies can be used as bases for the construction of these supramolecular systems through the adsorption of different molecules. SAMs are two-dimensional molecular structures, usually with a thickness between 1 and 3 nm, which can be precisely tuned by the molecular dimension and arrangement on the surface. In a typical SAM, molecules are bonded to the solid substrate by a reactive head that provides a strong molecule–substrate link to the system, while van der Waals forces among molecules stabilize the supramolecular assembly, introducing long-range or short-range ordering, depending both on the molecule and on the substrate. The molecular terminal group provides chemical functionality to the SAM and can be used to tailor the physical chemistry of the solid surface.

SAMs of thiol molecules on metal surfaces are the fundamental building blocks for creating complex structures by the so-called "bottom-up" approach. These SAMs can be easily prepared by using thiols (either aliphatic or aromatic), disulfides, thiosulfates, organic xanthates, and thiocyanates on single-crystal, rough or nanoparticle surfaces of clean metals, from both gas-phase and liquid-phase adsorption.

In particular, liquid-phase adsorption is an easy, low-cost, and low-temperature procedure that allows mass production and can be arranged over large substrate areas. The direct adsorption of electroactive species on a surface usually involves the synthesis of a sulfur containing derivative of the substance of interest. The immersion of the clean surface of the metal in an organic solution of the molecule of interest in a low concentration (usually between 0.1 and 1 mM) for a sufficiently long time that allows self-organization usually produces well-ordered modified surfaces. Examples are widespread in the bibliography and include metal surfaces functionalized with ferrocene, porphyrins, and metal redox-active complexes, among others.

Step-by-Step Functionalization of Surfaces

Another approach that has been taken to bind electroactive species covalently to a surface is to tether the redox probe to an already functionalized surface by means of a chemical reaction. This procedure is somehow similar to a synthesis, except that it takes place on the surface. One advantage to this method is that the purification steps are easier and mostly imply the thorough rinsing of the surface. One of its disadvantages is that complete functionalization of the surface is not always achieved.

This approach usually involves a first step where a bifunctional reagent (usually organic, alkylic, or aromatic) reacts through one end with the surface, leaving the surface with the desired functionality provided by the other reactive end. In a second step, the introduction of the desired electrochemical species can be achieved by post-functionalization. Many strategies can be (and have been) used for this purpose, regardless of the surface of choice (c. Au, Ag, Pt, Si, etc.).

The use of "click" chemistry or the formation of an amide bond are some of the possible chemical paths that have been used to post-functionalize a surface that already has an organic functional layer, and introduce a scientific meaningful function, such as an electrochemical or optical probe or bio-functionalization with different proteins, enzymes, DNA, and glycans, for example.

Functionalization of Metal Surfaces With SAMs of Bifunctional Thiols

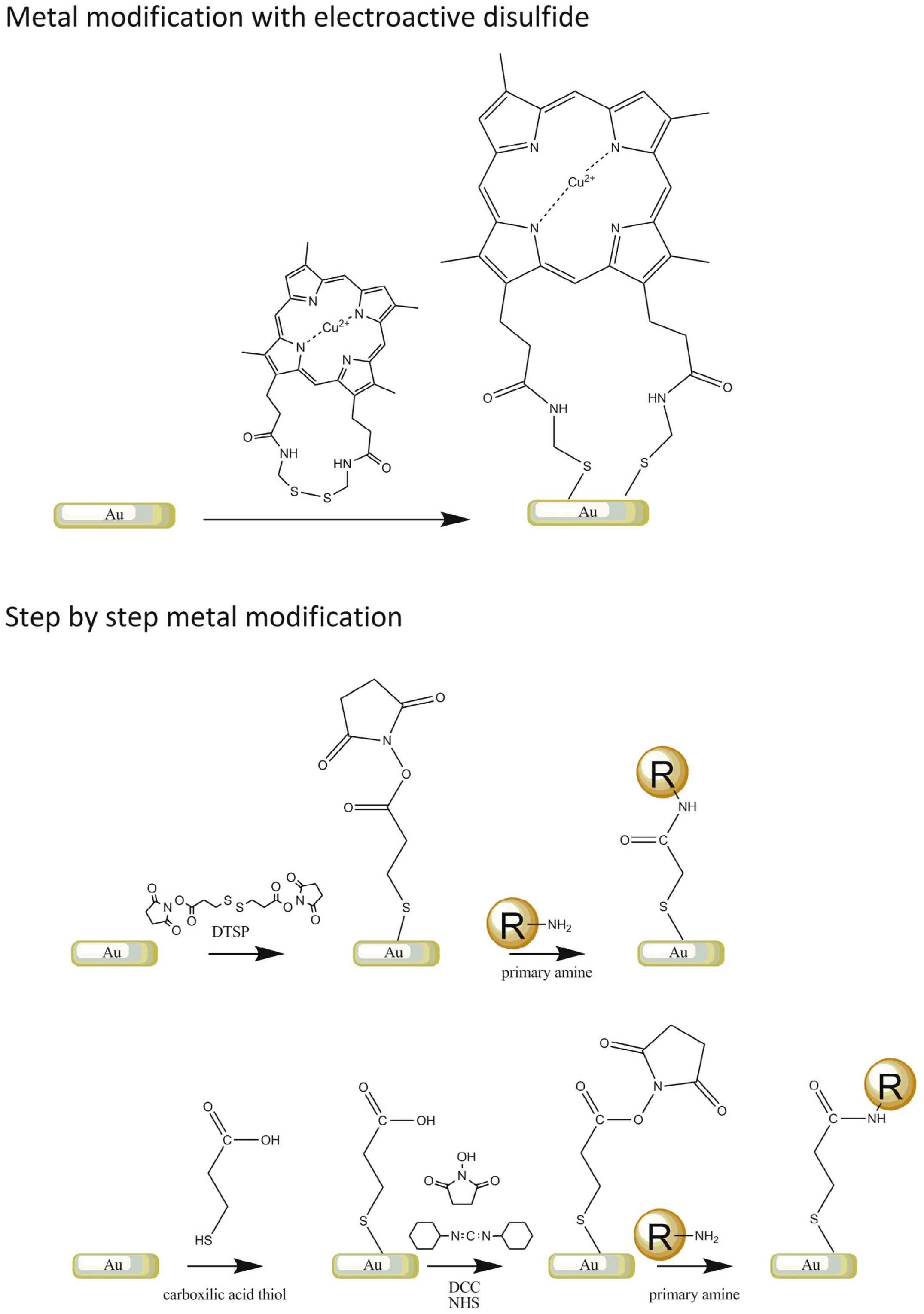
In this case, the first step is similar to the one described in the previous section. A bifunctional thiol bearing the desired functionality is self-assembled by immersion of the metal surface in a solution of the thiol.

In this way, towards further functionalization via an amide bond, metal surfaces are functionalized with a carboxylic acid thiol or dithiol. Afterwards, the carboxylic moiety is activated by immersion in an adequate carbodiimide and *N*-hydroxysuccinimide solution. If aqueous solution is to be used for the reaction, 1-ethyl-3-(3-dimethyl-amino-propyl)-carbodiimide is usually employed. Be aware that the pH of the solution may impact in the reaction performance. Usually a buffer of pH near 7 has been used. Frequently, these reactions are carried out in organic media, using an organic soluble carbodiimide, such as dicyclohexyl carbodiimide. After activation, the surface is incubated with the redox molecule of interest bearing a primary amine, and an amide bond is formed, covalently binding the redox active center to the surface. This approach usually results in a good yield, providing surfaces with high coverage of redox centers. It is possible to reduce the concentration of the redox centers diluting the concentration of carboxylic acid on the surface, in the first step, by self-assembling the bifunctional thiol with an alcanothiol, for instance. Scheme 1 shows the generalities of this functionalization path.

Another approach that can be taken, and has usually been used to tether enzymes to metal surfaces by some of its amine functionalities, is to incubate the surface with a thiol bearing an already activated carboxylic moiety, for example, dithiobis *N*-succinimidyl propionate. This method leads to a similar result on the surface as the previous one, and is also shown in Scheme 1.

A different pathway that has been used towards amide formation surface modification is to functionalize the surface with a primary amine, bearing in mind a subsequent activation of carboxylic groups present in the molecule of interest for further reaction with the surface.

Likewise, towards further functionalization via a copper catalyzed azide-alquine cycloaddition (CuAAC), "click" chemistry, metal surfaces have been modified with an azido moiety using an azido functionalized thiol. Once more, the surface preparation was achieved by immersion of a clean metal surface into an organic solution ~ 1 mM of the azido-funtionalized thiol, allowing


Metal modification with electroactive disulfide

Step by step metal modification

Scheme 1 Some pathways followed to modify metal surfaces with electroactive species (R).

sufficient time for the formation of an ordered monolayer (usually more than 10 h). Further reaction with the redox active species of interest bearing an alkyne leads to the sought surface. Copper sulfate and sodium ascorbate are often used as catalysts. "Click" chemistry-based reactions on surfaces are attractive because they bring together relatively small molecules that can be reacted to form a single unit utilizing chemically selective compounds and resulting in a high yield. These reactions occur under mild conditions and are tolerant to different chemical environments.

Electrochemical Grafting

Another approach that has been used to modify surfaces is the electrografting of the surface. It implies an electron transfer, and the substrate has to be connected to a potential generator. Electrografting applies to a variety of substrates including not only carbon, metals, and their oxides, but also dielectrics such as polymers. Since the 1980s, several methods have been developed, either by reduction or oxidation. Different reagents have been used for electrografting. These include amines, carboxylates, alcohols, Grignard reagents, vinylics, diazoniums, other ammonium salts, and halides.

Both oxidative and reductive electrografting can be performed. Oxidative electrografting can be performed mostly on materials that withstand oxidative conditions. It was first described on glassy carbon, carbon fibers and carbon felts and then on Au, Pt, and p-Si. Aliphatic amines have been oxidatively electrografted on carbon, gold, and platinum, leading to a substrate-N covalent bonding. Bifunctional amines, with a redox molecule of interest or a functional group to be further functionalized, were also used.

Reductive electrografting using aryldiazonium salts have attracted considerable attention for surface functionalization with covalent bonding at the substrate–aryl interface since Pinson et al. described the reaction mechanism for the modification of carbon electrodes by aryldiazonium salts in 1992. This technique can be applied to different materials: different varieties of carbon, semiconductors, gold and also Pt, Si, Fe, Cu, Co, Zn, and Ni. Therefore, this methodology constitutes a surface modification tool that can be applied in principle to all types of substrates. In this case, the electroreduction of a diazonium salt generates an aryl radical that can react with the electrode, forming a covalent bond with it. Therefore, it is an easy technique to implement, it generates stronger links between the substrate and molecules than the one obtained by thiol self-assembly, yielding films more difficult to desorb because of the strong metal–C covalent bond. It is not clear, however, that monolayers can be obtained in this way, since this method involves radical reactions and unless blocking of other possible reaction sites is performed, ramification of the monolayer is usually obtained, no matter how mild the applied reduction conditions are.

In spite of these difficulties, this method has been successfully used to tether derivatized aromatic molecules to the surface, following with the post-functionalization of the surface with electroactive groups, as described before.

Functionalization of Semiconductors

A number of approaches have been designed to form organic monolayers on semiconductor materials, with most efforts directed towards silicon because of its attractive semiconductor properties that can be easily tuned by doping, low cost, and easy of interfacing into existing electronic devices. The formation of molecular layers on crystalline silicon surfaces without an intervening oxide layer is an extremely appealing approach toward robust layers on a surface. The preparation of organic layers directly bonded to crystalline silicon surfaces has been receiving increasing interest because of its potential use in molecular electronics, as well as electrochemical and biochemical sensors. Silicon-carbon linked monolayers on silicon substrates are expected to complement and extend the applications of the currently most relevant technological materials towards the development of atomic scale devices. The ability to provide a chemically stable interface, without significant defect sites, is a central requirement for both, molecular electronic devices and sensing interfaces. Regardless of the chemical method used, the reaction between the hydrogen terminated Si surfaces must take place in an oxygen- and water-free environment, and usually requires elevated temperature or irradiation with UV/vis light.

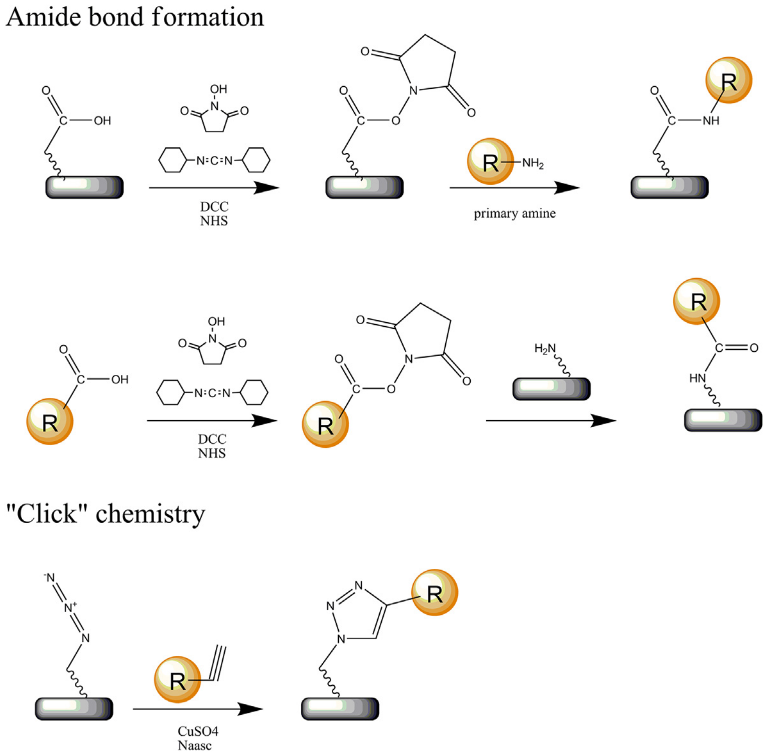
For attaching electroactive molecules onto oxide-free silicon surfaces, the most usual method involves the covalent reaction of bifunctional molecules with Si—H, which has been previously prepared by the etching of an oxide-covered silicon wafer in an aqueous containing fluoride solution (HF or NH4F). One of the functionalities of the molecule binds to the surface while the other is the redox center or a functional group that will be reacted in a subsequent step to introduce the desired redox moiety.

A very popular method for attaching organic layers to silicon uses the hydrosilation reaction with ω-substituted 1-alkenes or alkynes by thermal induction, ultraviolet light or catalysis. This method may produce electroactive centers covalently bound to Si through a Si—C bond. Often the electroactive center cannot withstand the strong chemical conditions needed for silicon modification. In these cases, a step-by-step modification is usually a good approach. The hydrosilation reaction has been proved efficient to produce carboxylic acid, amine, or azide functionalized Si surfaces, which may be subsequently modified, according to the adequate reaction, to attach an electroactive moiety, in a similar way to the previous examples. Scheme 2 shows some examples of possible ways of obtaining monolayers of redox species covalently bound, by step-by-step functionalization of the surface.

Electroactive Polyelectrolyte Layer-by-Layer Thin Films

Layer-by-layer (LbL) assembly is a method for coating substrates with functional thin films. It is usually a cyclic process that involves the adsorption of a charged material on a substrate, followed by the washing and subsequent adsorption of an oppositely charged material on top of this layer.

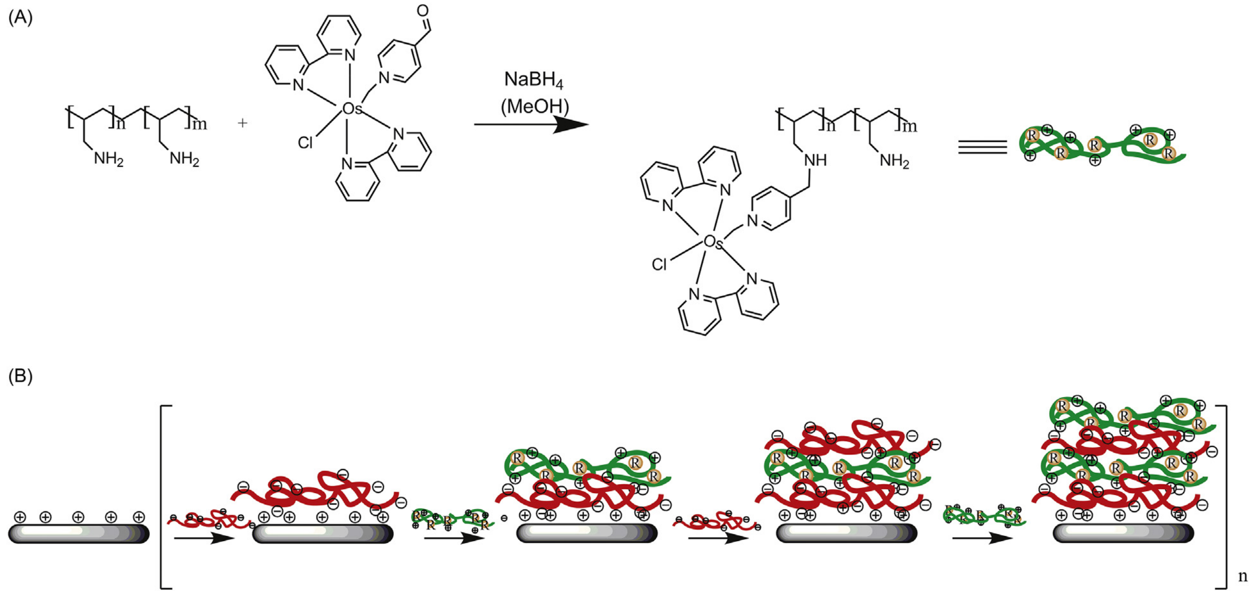
Electrode preparation by the LbL method starts with a metallic or semiconductor functionalized to bear a surface electrical charge. Thiols are usually used for gold or silver, silanes for Indium-tin oxide (ITO), and diazonium salts for carbon surfaces. The electrode is then immersed in a solution of an oppositely charged material, usually a polyelectrolyte that adsorbs on the surface. After rinsing, the electrode is dipped in a solution of another polyelectrolyte bearing an opposite charge. In each step the surface charge of the electrode changes so that these adsorption/rinsing steps can be repeated the desired number of times with the



Scheme 2 Some ways of postfunctionalizing surfaces to covalently bind electroactive species (R).

same or different polyelectrolyte. Typically each step is about a few nanometers thick. The films produced have an interpenetrated structure. Immersive assembly is the most commonly used LBL assembly technology because of its simplicity, although a number of other technologies are available, including spin, spray, electromagnetic, and fluidic assembly.

Electrochemically active or redox-active layer-by-layer polyelectrolyte multilayer self-assembled films on conductive substrates have been extensively studied because they exhibit a well-defined architecture and find applications in enzyme biosensors, perm-selective membranes, corrosion inhibitors delivered on demand, or precursors for metal nanoparticle formation and their use in



Scheme 3 An example of assembly of a layer by-layer polyelectrolyte electroactive thin film. Top: Preparation of poliallylamine covalently modified with an osmium bipyridine complex (also represented in *green*). Bottom: Schematic process of layer by layer deposition of this polycation (R = redox active group) and a polyanion (*red*).

electrocatalysis. These films can exchange electrons with the underlying electrode and propagate redox charge along the direction normal to the surface. The redox groups can be introduced by coordination, electrostatic binding, or covalent attachment to the polymer backbone. Some examples include the covalent attachment of an Osmium bipyridine complex to polyallylamine (see Scheme 3) and the introduction of the redox moiety by ion exchange after the layer-by-layer film was formed.

This strategy to modify electrodes with redox polyelectrolyte films has become an important tool for the fabrication of devices and electrodes. The unique possibility of controlling film thickness on the nanometer scale, the composition and thickness of each alternate layer separately, as well as the surface charge by choice of the topmost layer, allows the intelligent design of devices with important applications in biosensors, electrocatalysts, corrosion-resistant coatings, etc.

Final Remarks

The functionalization of conductive or semiconductive surfaces with redox-active monolayers or films is a powerful approach for the fabrication of smart interfaces with interest in applications such as electrochemical switchable molecular junctions, devices for information storage, electrochemical sensors and catalyzers. The actual application of these surfaces in usable devices requires high-quality surfaces that are chemically and electrochemically stable. Thus, efforts must be concentrated on controlling compactness and robustness of the layer and the surface covering of electroactive species.

See also: Chemical Functionalization and Surface Nanopatterning; EAB—Electroactive Biofilm: A Biotechnological Resource; The Dynamics and Characterization of Electroactive Biofilms.

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