

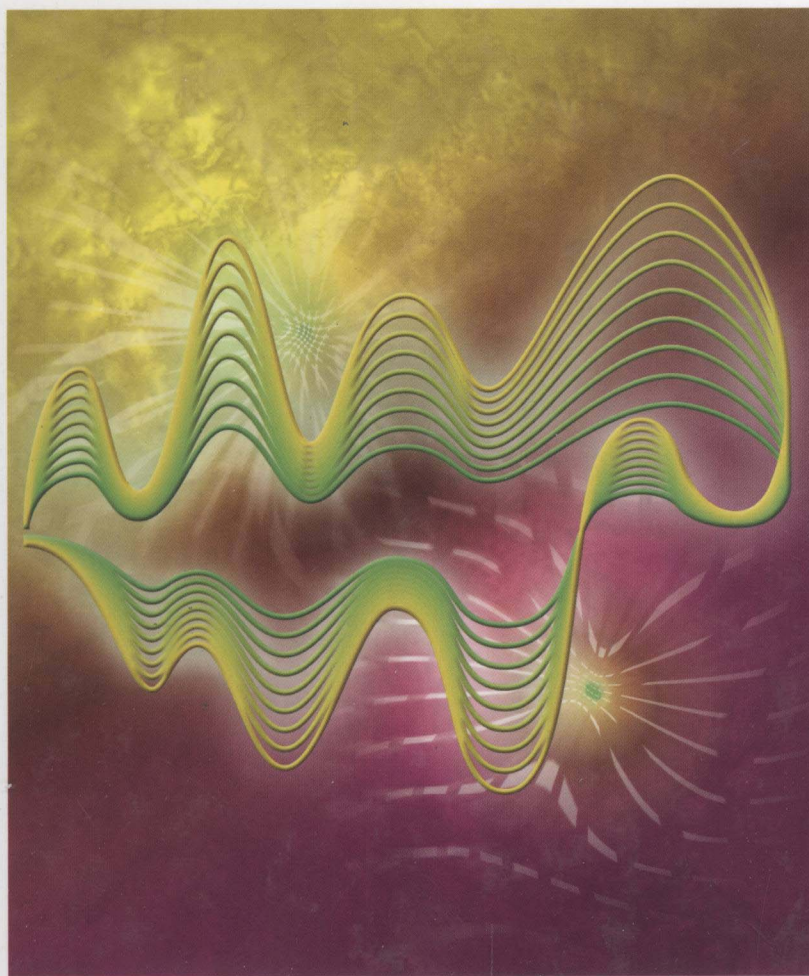
Advances in Electrochemical Science and Engineering

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Chemically Modified Electrodes

Volume 11



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Chemically Modified Electrodes

Edited by

*Richard C. Alkire, Dieter M. Kolb, Jacek Lipkowski,
and Philip N. Ross*



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**Advances
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Science and Engineering**

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Chemically Modified
Electrodes

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Preface

The steady expansion of interest in electrochemical science and technology creates the need for a monograph series of the highest standards for the experienced reader. The purpose of the *Advances in Electrochemical Science and Engineering* series is to provide high-quality advanced reviews of topics of both fundamental and practical importance.

The current volume addresses issues of chemically modified electrodes. Whenever bare surfaces do not fulfill the needs required, their chemical modification is a most promising way out of the dilemma. Purposeful attachment of atoms, molecules or even whole (nano)particles to the surface allows one to tailor the electronic and structural properties of a surface and hence, its functionality over a wide range. In the five chapters of this volume, internationally renowned scientists describe, how to modify a surface and what to do with it.

M. Buck reviews in great depth the literature on self-assembled monolayers (SAMs) of thiols on gold, a classic means of surface modification. The wide variety of functional groups that is provided by synthetic chemists makes thiol-SAMs an exciting playground for applications where the gap between two worlds, the inorganic and the organic, needs to be closed. Examples are molecular electronics and biochemistry.

M. Tagliazucchi and E.J. Calvo present another important and exciting means of modification: by electrochemically active polyelectrolytes. Polyelectrolytes modify surfaces by their inherent electric charges, which can be used, e.g., for constructing multilayer films of opposite charge, or simply by changing the electrochemical potential of reaction partners. Their role in many areas of chemistry, particularly of electroanalysis and biochemistry, cannot be overemphasized.

Carbon nanotubes are increasingly recognized as a promising tool for surface functionalization. M.J. Esplandiú presents a state-of-the-art overview of their applications in electrochemistry. As with SAMs of organic molecules the great potential of carbon nanotubes lies, among others, in biochemical applications and in molecular electronics.

Gold nanoparticles (NP) are just one of a variety of ways to modify the chemical behavior of surfaces by entities that can be described by their solid-state rather than

atomic or molecular properties. From D.A. Buttry's chapter it becomes evident that their potential is mainly in electrocatalysis, an area of vast practical importance.

J.J. Gooding *et al.* touch upon many of the above-described systems on their exciting tour through the field of nanostructured electrodes with unique properties, particularly for biochemical and sensor applications. Again, it is the intelligent design of a bridge between measuring devices and the living world, which is highlighted in this review.

The reader may notice many cross-references between the five contributions, which support the view that chemical modification of surfaces, particularly the nanostructuring, is not only interesting for its own sake, but also relevant to a wide range of practice applications. Their seminal role in bioelectrochemistry, bio-sensing, electrocatalysis and electroanalysis among others is clearly evident in this volume.

Ulm, April 2009

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1

Nanostructured Electrodes with Unique Properties for Biological and Other Applications

J. Justin Gooding, Leo M.H. Lai, and Ian Y. Goon

1.1

Introduction

Modifying the surface of electrodes to provide some control over how the electrode interacts with its environment has been one of the most active areas of research interest in electrochemistry within the last 30 years [1]. Whereas once the performance of an electrode was limited to the solution it was placed into, the material from which the electrode was made and the potential applied to the surface, the ability to chemically modify electrodes has provided a powerful route to tuning their performance. This has been particularly important to electroanalytical chemistry [2, 3], where modification has provided routes to providing selectivity, resisting fouling, concentrating species, improving electrocatalytic properties [4] and limiting access of interferences in a complex sample [5], such as a biological fluid, but has also had major impact for research into energy conversion [6, 7] and storage, corrosion protection [8], molecular electronics [9–11], electrochromic devices [12] and fundamental research into phenomena that influence electrochemical processes [9]. In recent years this revolution into tailoring electrode surfaces, such that the electrode has unique properties, has continued at an even greater rate with unprecedented control over the modification process via advances in nanofabrication. Taken in its broadest context, nanostructuring electrodes can be regarded as controlling the architecture of an electrode at the nanoscale; whether it be using nanomaterials, templating methods, organic monolayer modification of electrode surfaces or hybrid modification layers involving organic monolayers and nanomaterials. These different strategies for modifying electrodes provide opportunities to confer a unique range of properties to electrode surfaces from ultrahigh surface areas achieved with templated electrodes, to electrocatalytic properties with nanoparticles, strategies to achieve electrochemistry in locations too small for conventional electrodes, such as inside enzymes, and give electrodes with switchable properties.

Many of the unique properties that can be achieved with nanostructuring at the nanoscale are due to the ability of the unique properties of the nanomaterials employed, the ability to control the architecture of the electrode interface at the

nanoscale or both. This nanoscale design of electrode interfaces potentially provides spatial control vertically from the surface and/or laterally across the electrode surface. In many ways self-assembled monolayers (SAMs) and templated methods offer the greatest possible control over how an electrode interface is modified as the electrode design and properties are tailored at something akin to the molecular level [13–15]. This spatial control is coupled with chemical control via the ability to incorporate multiple chemical components into a single interface to provide the interface with a range of properties. An example of such control is in the ion-channel biosensor where up to 10 or more molecular components are incorporated into a lipid bilayer for modifying electrodes where both lateral and vertical control are required to give one of the most versatile and sensitive biosensing concepts ever developed [16]. It is this molecular-level control with monolayer technologies that also forms the basis of many unique nanostructured electrode concepts involving nanoparticles, nanotubes and other nanomaterials where self-assembled monolayers form the linker between a macroscopic electrode and the nanomaterial [14].

It is the unique properties that can be conferred to an electrode by nanostructuring using nanomaterials, self-assembled monolayers and templating methods, particularly with regards to a biological context, that are the subject of this chapter. The chapter is not intended to be a comprehensive review of all the work done on nanostructuring electrodes but rather to cover some of the recent advances in nanostructuring electrodes, which are important for using electrodes for biological applications. Firstly, strategies to produce electrodes with high surface areas and their applications in enhancing electrode sensitivity will be discussed. The discussion of surface area will be followed by the structuring of electrodes with nanoscale features that provide catalytic properties to the electrode. The third section will cover the small size of features providing the opportunity to intimately interface electrodes with proteins. This section will include using molecular wires to give blocked electrodes where electrochemical communication is maintained through molecular wires. The final section of the chapter will explore switchable surfaces where spatial modulation of the electrode modification layer is exploited to radically alter the properties of the electrodes. In all cases our emphasis will be on methods of electrode modification that are highly controlled.

1.2

High Surface Area Electrodes

Incorporation of nanostructures onto the surface of electrodes began in the early 1990s. These structures were initially used to enhance electrochemical signals due to their high surface-to-volume ratio. Gradually, work progressed to their application into bioconjugated systems. The increase in electroactive surface area allows for lower detection limits and higher sensitivity to analytes. This is demonstrated in the detection of H_2O_2 using films of nanoparticles in a three-dimensional structure [17, 18]. In these studies, multilayers of nanoparticles were built up with bridging molecules between the layers. The bridging molecules have redox-active

centers, which are sensitive to H_2O_2 . By having large areas of nanoparticle film, the number of redox-active centers increases, providing a more sensitive sensor compared with electrodes of the same material that do not comprise the nanoparticle films. The main challenge in achieving a high surface area electrode is the control over the size and distribution of the structures produced on the electrode surface. To accomplish this, the four main strategies in producing high surface area electrodes that have been employed are (1) the direct attachment of nanoparticles onto an electrode, (2) templating with membranes such as polycarbonates or alumina, (3) the use of lyotropic liquid crystals as templates and (4) colloidal templating. We will discuss each of these in this section.

1.2.1

Attachment of Nanoparticles onto Electrodes

Increasing the electroactive surface area has been successfully achieved by the attachment of nanoparticles onto an electrode. Natan and coworkers [19] pioneered this approach, where the initial idea was to attach nanoparticles onto a platinum surface to enhance electrode performance. In this first study the surface of a platinum foil was coated with a polymer, (3-mercaptopropyl) methyltrimethoxysilane (MPMDMS). Subsequently, the modified electrode was placed into a solution of 15-nm diameter Au nanoparticles. The MPMDMS and Au nanoparticle-modified layer was electrochemically active to the redox-active species, methyl viologen. An important observation made by Natan and coworkers [19] in this work is the electrochemistry was blocked when the Pt foil electrode was modified with the MPMDMS in the absence of Au nanoparticles but was 'switched on' when the nanoparticles were present. This demonstrates that the Au nanoparticles act as electrodes. However, when the oxidation and reduction peaks in the cyclic voltammogram (CV) were compared to a bare platinum electrode, the peaks in the CV of the nanoparticle-modified electrode had a slight broadening. The broadening was attributed to a closely spaced array of nanoelectrodes. Although this paper did not explore the effect of multilayers of nanoparticle films, nor the enhancement of the electrochemical signal provided by the increased surface area, this work paved the way for further investigation into nanoparticle-modified electrodes in general and for sensing in particular.

Following the lead of Natan and coworkers, further studies have demonstrated the ability of nanoparticles to enhance sensitivity by constructing multilayer structures composed of nanoparticles. Multilayers of nanoparticles linked together with conductive species create large internal surface area, which can be accessible to redox probes. The multilayered systems effectively create a porous network providing much higher surface area than a monolayer. For example, Blonder *et al.* [20] have modified indium tin oxide (ITO) electrodes with multilayers of Au nanoparticles. In this example the ITO surface was first modified with triethoxy aminopropylsilane in toluene, followed by the attachment of 12-nm nanoparticles (Figure 1.1). This nanoparticle-modified layer was then further functionalized with *N,N'*-bis(2-aminoethyl)-4,4' bipyridinium, a redox-active bridging molecule. Four layers of

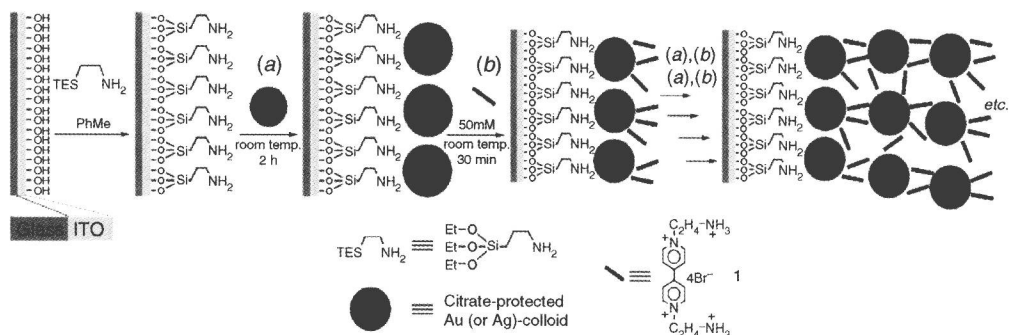


Figure 1.1 Stepwise production of metal-particle multilayer arrays. The attachment of the Au or Ag nanoparticles onto ITO-modified glass was achieved by using silanes that have an amine terminus group. This modification step allows for further modification with nanoparticles onto the surface of the ITO. After the nanoparticle attachment a redox-active bridging molecule was

assembled onto the Au or Ag nanoparticle monolayer. This step was repeated a number of times to produce a three-dimensional array of nanoparticles that has large internal surface area and increased redox-active species concentration. (Reproduced by permission of The Royal Society of Chemistry from [20].)

nanoparticle films were constructed by repeating the exposure to Au nanoparticles and the redox bridge. This study demonstrated that, as more nanoparticles were placed on the electrode, an increase in peak current was observed for the oxidation and reduction, when a cyclic voltammogram was taken in phosphate buffer at pH 7. The increase in signal was attributed to two related factors. The first was the increase in the number of redox molecules in the layer and the second was the increase in electroactive surface area.

The main idea demonstrated by Willner and coworkers [20] is the ability to construct multilayered nanoparticle electrodes, which are porous. In a related study Patolsky *et al.* extended this idea further using biocatalysts to detect H₂O₂ [18]. In this example, the construction of the electrode is similar to the one described above but the redox-active bridging molecule was replaced with microperoxidase-11 (MP-11).

MP-11 is an 11 amino acid long chain, with the heme center of cytochrome *c* (Figure 1.2), which is produced by proteolytic digestion. It is an electrocatalyst and biocatalytic unit for H₂O₂. By keeping the concentration of H₂O₂ constant at 0.5 mM and changing the number of layers of nanoparticles and MP-11, Willner and coworkers [18] observed the enhancement of peak current as the number of layers of nanoparticles and MP-11 deposited on the electrode was increased. Therefore, Willner and coworkers concluded that the three-dimensional structure can provide a tunable and sensitive sensing interface for H₂O₂ by adjusting the amount of nanoparticle layers present in the three-dimensional structure.

Electrodeposition is an alternative way to produce nanostructures on an electrode surface from solution onto a surface. Using electrodeposition to construct nanostructures allows for greater control over the amount of material deposited on the surface due to the ability to precisely control the charge that is passed into the system. Some control over the morphology is also afforded. For example, Liu *et al.*

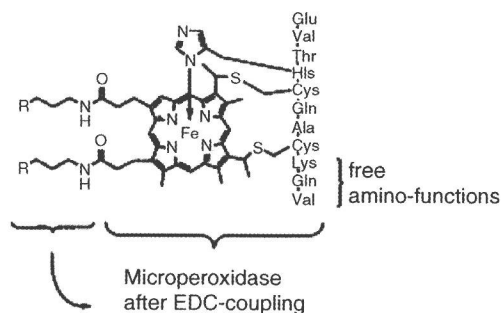


Figure 1.2 Stepwise assembly of MP-11, Au nanoparticle superstructure on ITO. (Reprinted with permission from Ref. [18]. © 1999 Elsevier.)

demonstrated the production of pyramidal, rod-like and spherical Au structures on Au foil [21]. The production of these nanostructures was simply achieved by electrodeposition of gold from an aqueous solution of 0.1 M HClO_4 and different concentrations of HAuCl_4 . For example, to produce pyramidal structures 40 mM HAuCl_4 was used and deposited at -0.08 V vs. $\text{Ag}|\text{AgCl}$, to produce rod-like structures 4 mM HAuCl_4 and -0.08 V vs. $\text{Ag}|\text{AgCl}$ was used and finally spherical structures were produced with 40 mM HAuCl_4 at -0.2 V vs. $\text{Ag}|\text{AgCl}$. After the formation of the nanostructures the surface was modified with Cu, Zn-superoxide dismutase (Cu, Zn-SOD). The enzyme immobilization was achieved simply by adsorption. The resulting electrodes were exposed to superoxide (O_2^-) and exhibited an improvement in the direct electron transfer between the SOD and the gold nanostructures compared with an electrode without nanostructuring. In particular the spherical nanostructured electrode showed excellent analytical performance, such as a wider linear range (0.2–200 μM), a lower detection limit (0.1 μM), a shorter response time (4.1 s) and a higher stability compared with the pyramidal and rod-like nanostructures.

The observation made by Natan and coworkers [19] that electrochemistry at a Pt foil electrode modified with the MPMDMS was dramatically altered when nanoparticles were present was also the first example where nanoparticles were used to alter the resistance of polymer films. At a similar time, Murray and coworkers [22] used nanoparticle films to explore the resistance properties of films relative to the length of the species that were used to bind the nanoparticles together into films. In this first study the modifiers were octanethiol, dodecanethiol and hexadecanethiols. The modified nanoparticles were produced by the reduction of HAuCl_4 in toluene followed by extraction into toluene where a molar equivalent amount of the thiol was added. The gold nanoparticles were flocculated to give a nanoparticle film. Conductivity of the films was measured and Murray and coworkers [22] reported a significant decrease in conductivity (150 times when compared between octanethiol and hexadecanethiol) as the length of the monolayer coating the gold nanoparticle increase. This unique ability of the dependence on length of monolayers on nanoparticle surface on resistance has been used to detect gaseous analytes.