

# The evolution of amperometric sensing from the bare to the modified electrode systems

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Received: 25 January 2011 / Accepted: 21 February 2011 / Published online: 6 April 2011  
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**Abstract** The article aims at giving a critical overview of the passage from bare to modified electrode systems, proposed for amperometric sensing. An introduction is made with reference to the development of modified electrodes since the beginning, i.e. from the 1970s. A

subsequent time border is arbitrarily identified around the middle of 1990s. Since those years, many novelties, coming in part from chemistry and in big part from physics and engineering, induced deep changes in the approach to the electroanalytical research; they are tentatively outlined. The term “research” is intentionally used to underline that wide room is still available to applications, waiting for efforts by electrochemists. It is also emphasised that the nature of the modifying systems has been only occasionally tailor-made, i.e. designed and developed on purpose. A strict enough connection between the electrochemists and the chemists expert in synthesis has been and still is often scarce. This notwithstanding, the number of novel potentially interesting materials suitable to develop electroanalytical systems highly effective in applications is so high that the next future of electroanalysis seems definitely promising. A brief critical analysis of electrode systems based on similar materials is made.

**Keywords** Electroanalytical chemistry · Electroanalysis · Amperometric techniques · Sensors · Electrochemical sensing

## Introduction

We do not aim at writing either a story (!) of electroanalytical chemistry or a short review on recent progresses in amperometric sensing. We rather aim at pressing for a discussion about the issue; the “historical part” of the draft constitutes hence a sort of introduction to a tentative envisioning of the next future: we believe in fact that, for this purpose, it is useful to briefly trace the path through which electroanalytical chemistry has arrived to year 2011. The lost occasions and the still widely open doors, often due to electrochemists’/electroanalysts’ fault, will be evidenced more than the successes. We firmly believe that there are many possible directions on moving our efforts in

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order to make electrochemistry competitive with respect to other analytical techniques. This is why weakness together with strength points of the recent work in the field are tentatively picked up.

Our attention is mainly oriented to the electrode materials due to the fact that they are the main object of the electrochemical research nowadays, and supposedly will be in the next future. It is more difficult to think that new techniques may constitute a sound breakthrough in a short time. Other tools, from novel instrumentation to modelling software, have been in the past and will be in the future made available by chemists, physicists, biologists and engineers. It will be for electrochemists to pick up and exploit them at best.

Talking of electrode materials, Hg was the metal that in the 1940s pushed electroanalytical chemistry to highest consideration in the field of electrochemistry and even in that of chemistry as a whole. In addition to the huge amount of experimental work made with this unique metal, polarography also constituted the experimental benchmark for the enormous theoretical work dealing with any sorts of electrode mechanisms. Since then, this work has been the basis of molecular electrochemistry, and not only of it. The unprecedented School of Prague had “founded” polarography or voltammetry when intended as the ensemble of techniques devoted to obtain current vs. potential curves.

In the (fabulous) 1960s, music changed in any fields: the era of solid electrodes had begun. On one side, it is not risky to affirm that Paul Delahay’s book published in 1954 [1] opened the door to diffusion of the voltammetric techniques. On the other side, Heyrovsky’s and Kuta’s “polarographic bible” [2] constituted a sort of finish line for the Hg electrode (however, do not forget the more or less contemporary textbook by Koryta et al. [3]), while in 1969 Ralph Adams published the volume [4] that constitutes a reference point for different electrode materials than Hg. These were, at that time, Pt, Au and various forms of C. Nor is a chance that in 1966 the first volume of the Bard’s series of monographs entitled *Electroanalytical Chemistry* [5] was published.<sup>1</sup> Of course Hg was still taken into great consideration also in the 1970s, 1980s and even nowadays, but many competitors appeared, and more and more rigid rules about toxic chemicals induced to progressively reduce its use. Moreover, the development of new sophisticated electrochemical instrumentation allowed the electroanalytical chemists to propose new electroanalytical techniques.

<sup>1</sup> It should be incidentally evidenced how the Bard’s series defined the meaning of the discipline “electroanalytical chemistry” in a wider sense, including topics that are not directly linked to analysis in the strict sense. As chemists bearing the label of “analytical chemist”, though being actually interested in any aspects of the system realised, we are very keen on defending such a view. We do not know how crowded the club is nowadays.

In the 1970s, one assisted at a rush toward oxidation studies and toward rigorously anhydrous nonaqueous solvents, capable to “unreactively” dissolve organic molecules, and even coordination and organometallic compounds. Voltammetry at solid electrodes with periodical renewal of the diffusion layer was proposed to substitute for polarography, although, obviously, the “history” of the electrode was well present on the solid surface. Better performances were reached with the rotating disc electrode and with pulse techniques on solid electrodes, which are still well alive nowadays. However, linear sweep and cyclic voltammetries played the main role, also thanks to the favourable information content-to-effort ratio. The 1960s and the 1970s were also the decades in which theoretical studies considered all sorts of complex electrode mechanisms, also thanks to the shorter and shorter time windows allowed by linear sweep and cyclic voltammetry, as well as by chronoamperometry.<sup>2</sup> The theoretical time window was pushed down to such low values to be actually far too difficult to reach experimentally. Sophisticated theoretical treatments of the various DC-controlled potential techniques, and even of AC voltammetry, higher harmonics included, dealt with every possible (and even impossible...) sort of mechanism. The development of microelectrodes was experimentally of some help with this respect, opening unexpected possibilities to the study of extremely fast chemical reactions coupled to the charge transfer(s).

Digital simulation techniques, first introduced in electrochemistry by Feldberg [6], were of basic importance for the theoretical elaboration of responses. Later on, they were also inserted in commercial packages that, when used by those who were/are familiar with the content of the black box, resulted to be helpful.

It is worth and proper to incidentally underline that studying and researching in molecular electrochemistry, also when the realisation of suitable experimental conditions was so difficult to achieve, constituted and still constitutes an invaluable way of acquiring knowledge in dynamic electrochemistry and even electroanalytical chemistry. It still continues to be an invaluable tool also after the electrode systems have shifted to higher complexity and the deep elucidation of complex electrode mechanism does not constitute the key point of the study anymore.

More recently, different needs from theoretical studies considering every possible complex mechanism arose. They were even practical, thanks to progresses in other disciplines.

<sup>2</sup> It is hard to pick up the most significant articles, from those of Matsuda and Ayabe, and of Nicholson and Shain, to those of Saveant and the school in Paris. Many other big names of electroanalytical chemistry were active in theoretical work those years, building the basis of modern molecular electrochemistry and of electroanalytical chemistry as well.

As a consequence, both experimental and theoretical efforts shifted for the most part to studies of different complex systems, in which a variety of more or less conductive materials are interposed between a conductive substrates and the environment. Electroanalytical chemistry became more and more oriented toward true analytical aspects (*electroanalysis*) and the appealing term *sensing* became particularly on the rise. The change in terms sometimes hid/hides the “it works” approach that so often induced/induces to consider electrochemical methods as mere tools for building more or less reliable regression lines by more or less correctly exploiting differently collected currents.

It seems important to notice that the introduction in electroanalytical chemistry of novel electrode materials with respect to Pt, Au and C, as well as to Hg, only in part exploited what already developed in other fields of electrochemistry, such as in electrosynthesis or in batteries and fuel cells. Similarly important is to evidence that such a “transfer of expertise” was intentionally addressed by precisely identified visions of the goals to reach. The principal scopes pursued by modification of an electrode to use for electroanalytical purposes were identified since the very beginning and were/are: (1) to activate (selective) electrocatalytic processes, (2) to prevent fouling of the surface, and (3) to (pre)concentrate selectively the analyte under exam close to the electrode.

Selectivity is an intrinsic property of the electrode as a reducing or oxidising agent since the energy, i.e. the electrical potential, necessary to induce charge transfer, is a more or less specific property of the different chemical species: the modulation of the electrode potential makes it “selective” for the species electroactive at the polarisation potential. However, it often happens that such a selectivity factor is not sufficient since electroactive species present in the same solution may undergo charge transfer at too similar potentials to give resolved responses. Electrocatalysis may shift one response with respect to the other, as well as allow electrode reaction to occur in charge of species that are otherwise redox active beyond the solvent discharge. Selectivity by what is actually a true chemical catalysis may also be achieved by anchoring chemicals or functional groups at the electrode, suitable to differently interact only with given species: catalysis may occur favourably altering the energy path from reactant to product of the charge transfer.

On the other hand, it is well known that many species exhibit affinity to metal and even C surfaces, leading to more or less strong adsorption on them, often implying more or less strong poisoning that hinders electron transfer. It happens that electrode coatings suffer less from fouling adsorption, anyway allowing the charge transfer to occur. A challenging task lies in coupling the two effects, also in the frame of electrode systems composed by different materials, aiming at joining and, possibly, even enhancing the favourable features of the individual components.

A further goal envisioned when modifying properly an electrode surface may be that of increasing the sensitivity of the responses by pre-concentrating the analyte close to the electrode surface. In most systems developed, such as ion exchange polymers, only small changes in the thermodynamics of the charge transfer with respect to the situation in solution are induced.

Among the unconventional approaches that were developed since the beginning of the employment of electrochemistry for analytical purposes, microelectrodes deserve specific attention [7]. They most often consist of metallic or C microdiscs; the peculiar diffusion regime to the electrode surface, quite different with respect to the case of conventional electrodes, allows their use in poorly conductive or highly viscous media. This notwithstanding, they were not widely used in similar context, and even much less analytical applications of modified microelectrodes are found in the literature [8]. On the other hand, a number of applications are found that exploit the possibility of using them as poorly invasive, highly localised probes [9]. A further unconventional approach is represented by the coupling of optical techniques with electrochemical ones in order to either enhance or tune the response of the whole sensing system [10].

### **The second electroanalytical era. The first 30 years of electrode modifications, i.e. from the 1970s to the sunset of the 2nd millennium**

After the first approaches to modification of electrodes [11–13],<sup>3</sup> short reviews on the novel topic appeared at the very end of the decade [14, 15]. Sufficient amount of work in the field had already been made in 1984 to induce Royce Murray to authoritatively make the first exhaustive point in an excellent chapter in the frame of the Bard’s *Electroanalytical Chemistry* series [16].<sup>4</sup> In his review, Murray gives a sort of definition of what a modified electrode is intended to be, by means of the role it is claimed to play: “...one

<sup>3</sup> The references given are incredibly far from being exhaustive. Most probably, also the effort to pick up the most significant steps of the evolution, in terms of both single articles and authors, failed. The bibliography reflects a choice, among the huge amount of literature R. S. collected in so many years, that is often biased by personal familiarity with given articles.

<sup>4</sup> It seems significant that, in the same Volume, a Chapter deals with “polynomial approximation techniques” in the simulation of complex electrode processes in solution phase [17]. The treatment pays particular attention to any possible homogeneous events coupled to the charge transfer(s), though electrode systems different from bare conductors are, quite reasonably, not considered yet. As to the authors of these pages, R.S. had stopped taking care of finite difference simulation algorithms [18, 19], erroneously estimating that the most part of the work in the field had been already done. That’s one reason why, thinking at the “future” issue of the present volume, R.S. decided also to involve a young co-worker (co-author F.T.).

deliberately seeks in some hopefully rationale fashion to immobilize a chemical on an electrode surface so that the electrode thereafter displays the chemical, electrochemical, optical, and other properties of the immobilized molecule(s) (...) one selects immobilized chemicals on the basis of known and desired properties (...) the electrode can be tailor-made to exhibit these properties". Chapeau! Especially for the use of the specification "in some hopefully rationale fashion", which is not often suitably considered by the researchers working in the field, in particular when not particularly experienced in electrochemistry/electroanalysis. It is difficult to find meaningful changes to such a definition even after 27 years have passed. The list reported is suitable to perfectly envision what would have to be done in the next decades. Unfortunately, the final statement, according to which "the electrode can be tailor-made to exhibit these properties", has been too often interpreted with particular emphasis to the "can" verb, rather than to the "tailor-made" adjective: it is not frequent at all to find studies in which the problem of the estimation of a given analyte addresses the development of a more or less specific electrode material. Much more frequent is the case of a wide variety of materials proposed to more or less effectively determine the same analytes. In other words, Murray's auspice [20]: "One of the beauties of the CME [Chemically Modified Electrode – R.S & F.T.] idea is that it leads the chemist to rationally draw 'paper scheme' designed to produce certain type of electrode behaviour, using energetic and dynamic ground rules no more complicated than those of spectroscopy and photochemistry" is still largely unrealised. It is evident that a strict enough connection between (organic) synthesisers and electroanalytical chemists, despite a very promising start of the adventure [21], has not been activated; the pipeline often stops at the electrochemical characterisation of the systems realised, rarely, if ever, being capable to activate a feedback "on purpose" action.

Chemisorption should be considered the first pursued procedure followed to immobilise chemical species at a conductive surface. In the very most cases they consisted of  $\pi$  systems containing functional groups suitable to interact more or less selectively with species in solution [11, 12]. Modification by monolayers on conductive surfaces exploited the studies made in preceding years on adsorption [22]; such an approach typically leads to partial or complete coating by one single monolayer of molecules. Chemisorbed unsaturated molecules were studied also considering them as species suitable to activate electrocatalytic charge transfer processes, which were not, however, exploited in an analytical context. Both Co porphyrin and phthalocyanine were adsorbed on Pt or C surfaces to catalyse  $O_2$  reduction. Particularly elegant is the mechanism through which on purpose designed and

synthesised dicobalt face-to-face porphyrins resulted effective for this purpose [21, 23].

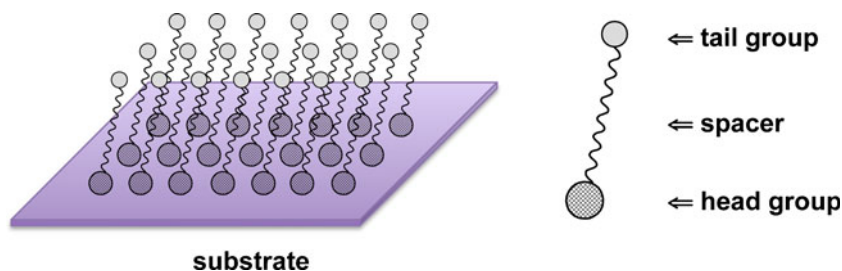
The stability of the systems realised by such an approach is, however, questionable, and modification of specific molecules by covalent bonding, exploiting anchoring groups such as Pt–OH or different C–O functional groups, either present spontaneously or created by oxidising agents on Pt, Au or C surfaces, was soon preferred. Among the procedures exploiting functional groups on the substrate surface in order to form true covalent bonds, silanisation of a number of oxide surfaces was quite a diffused practice [24, 25]. The species containing silane as the anchoring residue were further linked to a variety of other species through a second functional group, giving rise to a wide number of structures on the electrode substrate, polymers included. A wide series of metal complexes were also fixed at a surface by such an approach; however, the interest was mainly devoted to the study of the redox properties, namely of the formal potentials, of the complexes in such a condition, in comparison with the same complexes in solution. The potentiality of silanisation was strongly limited by the necessity to use rigorously anhydrous media in order to avoid oligomerisation in solution of the residues to anchor, as well as to obtain stable anchoring.

Also, depending on the nature of the substrate conductive material, many different alternatives to silanisation have been proposed. As an example, by thionyl chloride activation of a C substrate, a variety of metal porphyrin complexes, also bearing different ligands in the axial positions, were realised and anchored to the substrate, hence modulating the redox mediating characteristics of the developed electrode systems. Interestingly, it should be cited that thionyl chloride was also used in the realisation of chiral active surfaces [26] suitable for enantioselective synthesis and even—why not?—sensing. Unfortunately, these attempts only were of limited success.

It is noteworthy that the term self-assembled monolayer (SAM) appeared in the electrochemical literature only later, becoming then progressively more and more diffused when aiming at realising monolayers anchored at the substrate (Fig. 1). Much less diffused was the approach based on Langmuir–Blodgett layered systems. After pioneering works devoted to the development of SAMs [27–29], the proposal of thiol heads for (stable) anchoring was not enthusiastically welcome. The tunnel effect was identified as the responsible for charge transfer between the conductive substrate support and, through the spacer, the outmost part (tail) of the SAM structure, till to the redox species in solution [28, 30].

Later on, by deposition procedures combining chemisorption with low solubility of pure organic or metal-containing polymers, films as thick as a few micrometres were built up. Once more, at the end of the 1980s, the

**Fig. 1** Typical structure of a self-assembled monolayer (SAM). The head group can be anchored to the substrate through chemisorption or covalent bond



possibility of imparting a certain degree of order to multilayer systems by the Layer-by-Layer (LbL) deposition technique, in which at least one of the components in the two-component structure is a polyelectrolyte, was claimed [31]. Actually, it is well known that the interpenetration of adjacent and even non-adjacent layers makes similar systems far from possessing ordered structures.

Polymer-coated electrodes were proposed at the end of the 1970s [32, 33], essentially limited to redox polymers, ion exchange polymers or permselective coatings. A number of redox polymers exploit the reversibility of different redox couples of Ru complexes [34]; Ir, Os and Re complexes, as well as ferrocene [32], were also linked to different polymeric chains. In particular, Ru and Fe complexes bearing vinyl-substituted ligands were also polymerised by cathodic reduction [35]. The different characteristics of the redox changes involved in the self-exchange reactions, which are responsible for charge percolation through redox polymers, were nicely evidenced in Ref. [36], by comparing the Co(II)/Co(I) and Co(III)/Co(II) redox couples. Organic residues suitable to give reversible redox couples were also called to play the role of both charge carriers inside the deposit and of redox mediators at the interface with the solution. Among these, let us recall quinones and viologens. It should be noticed that 4-nitrostyrene [33] and dopamine polymers were among the first redox polymer coatings shown to exhibit effective electrocatalytic properties. It should be, however, kept in mind that electron hopping between two adjacent redox centres requires migration of counterions inside the polymer mass and redox centres close enough to each other, at the same time; the conductivity of the film is affected by both of these factors.

As an effort to overcome the latter possible drawback, metal complexes were also anchored on substrate surfaces by electrostatic binding through polyelectrolytes [37]. Thanks to the mobility of the ions involved, the charge percolation by self-exchange redox reaction is easier in similar systems than in the classical redox polymers. Both anionic (Nafion<sup>®</sup>) and cationic [38] polymers have been proposed, either aiming at fixing redox mediators or at pre-concentrating ionic species to strict analytical purposes [39].

Porphyrins and metalloporphyrins deserve a specific citation. Quite interestingly, in a series of articles appeared

in the second half of the 1980s, four substituents at the porphyrin rings were aniline [40, 41] or 1-pyrrole moieties [42]. By anodic oxidation, porphyrin and metal porphyrin substituted polyaniline and polypyrrole electrode coatings are obtained, characterised by a mixed electronic and redox conduction. These classes of materials are called *metallopolymers*. The era of conducting polymers had begun, and electrochemists at the frontier of research, possessing highest background electrochemical (and chemical...) culture, coupled to outstanding imagination and creativity, already developed electrode systems with properties that are often unmatched nowadays.

Shifting to pure inorganic materials, various metal hexacyanoferrates have been differently precipitated onto electrode substrates, acting as effective redox mediators. The first compound of this class proposed was Prussian Blue ferric ferrocyanide, which is both reducible to Fe(II)Fe(II) and oxidisable to Fe(III)Fe(III) [43]. Further inorganic coatings, such as montmorillonites [44] and zeolites [45], were used to fix electroactive inorganic or organic cations, even to use as redox mediators. Few years later, also hydrotalcites and hydrotalcite-like clays [46] were proposed for different electrochemical scopes, such as including redox species or transition metal ions, aiming at promoting electrocatalysis. Finally, polyoxometallates have been widely investigated, even for electroanalytical purposes [47].

Some of the systems described above can be defined as *hybrid materials*, intended as “materials composed of an intimate mixture of inorganic components, organic components or both types of component” [48]. An important class of hybrid materials developed in those years are actually *composites*, i.e. “multicomponent materials comprising multiple, different (non-gaseous) phase domains in which at least one type of phase domain is a continuous phase” [48]. The pioneering studies were at the embryonic state when compared to the astonishing advances gained in the recent past (see next section). At that time the preparation and characterisation techniques were still at the beginning or even they did not exist yet at all, as an example, scanning probe microscopies were invented only at the beginning of the 1980s.

This notwithstanding, in the very largest portion of the articles, the attention was essentially devoted to the

characterisation of the deposit, although essentially based on electrochemical techniques. To these, highest faith was given, even to draw out conclusions about structural properties. In a much lower number of cases, the electrocatalytic capability of the modification was checked with respect to species in solution, however, often far from constituting a proper electroanalytical task. Rare and isolated cases of efforts toward applications in electroanalysis that take care of effectiveness in calibration, sensitivity and selectivity of the proposed systems should be dated to the middle of the 1980s. In Refs. [49, 50] suitable functionalised polymer films bear ligand groups specific to a given metal ion. Further examples are just occasional in the subsequent 10 to 15 years. A limited literature dealt with composites that, in the frame of electroanalysis, normally employed C-based particles [51, 52]: as a few meaningful examples, herbicides have been quantified through a graphite–PTFE mixture [53]; L-cysteine has been quantified using a mixture of Kel-F, C black and Co phthalocyanine [54]; and Pt/C/wax composite has been employed for the determination of hydrazine [55].

Interestingly, electrochemical detection in liquid chromatography and electrophoresis became more and more popular, suitable for the determination of a number of different analytes. However, the majority of the electrodes used in these systems were and still are based on Au, Pt and C-based bulk materials. Surprisingly, the use of modified electrodes is relatively rare, normally limited to basic research studies [56].

As a final consideration, it is worth noticing that the modification of electrode surfaces with biological materials, in particular with enzymes, began quite early. The seed activity was carried out by Clark in the 1960s [57], as an evolution of his studies on the well-known O<sub>2</sub> amperometric sensor.

The 1990s were definitely the years in which modification of electrodes with electroactive layers assumed prominent role in electrochemistry. In the last 20 years, we assisted at an explosion of new electrode materials. Literature reports literally hundreds of new systems anchored to the electrode. However, in the very most cases, they are once more just proposed and characterised in their essential aspects. Much more rarely, they are fully characterised; in an even lesser number of studies, they are characterised as to their behaviour in applications, though essentially in electrochemical applications different from analysis, such as fuel cells, electroremediation, etc. The number of systems studied with respect to the electroanalytical properties is really discouragingly low; in addition, in most cases, the same benchmark analytes are explored in order to define the characteristics of the novel systems proposed. Tens of articles (we are among the authors of some of these...) test the selectivity of the electrode systems developed with respect to the ascorbic

acid/dopamine mixture in buffered solutions, very often avoiding more complex matrices, either real or synthetic ones.

### The present, i.e. the last 15 to 10 years

In the second half of the 1990s, we assisted at a further step in the evolution of electrochemistry that, in a way or another, can be connected to electroanalysis. The main factor inducing the step consisted in the availability of new tools to electrochemists. The list is long, often based on or connected to the explosion of electronics. The old, often home-made potentiostats, though very sophisticated and really revolutionary in some cases [58], were progressively substituted by commercially available systems controlled, both in input and in output, by more and more powerful software. On one side, this opened non-electrochemists the way to work in electrochemistry, sometimes leading to interesting results, though sometimes requiring careful reconsideration. On the other side, portable electrochemical instrumentation became soon available at quite reasonable prices, in principle allowing electroanalysts to propose electrochemistry as a powerful tool for “in field” analyses, being definitely competitive with respect to techniques requiring heavier, bulkier, more delicate and more expensive instrumentation. Remote control via wireless communication also became well practical. Amperometric sensing has also met with some of the industrial requirements in process control. As an example, companies active in the field of electroanalysis recently commercialised totally automated systems for on-line analysis of real matrices, which can be easily integrated in industrial plant [59]. At the same time, sophisticated spectroscopic and microscopic instrumentation became more and more easily accessible, encouraging deep characterisation of the electrochemical systems realised. As to techniques suitable to characterisation of electrochemical systems and to couple with electrochemistry, see, among others, the book series *Electroanalytical Chemistry*, edited by Allen J. Bard et al., 23 volumes from 1966 to 2010 and *Modern Aspects of Electrochemistry*, 51 volumes with various editors, from the 1950s to nowadays.

Miniaturisation constituted and still constitutes a further impulse to new frontiers. It allows the realisation of reproducible commercial microelectrode systems, e.g. by lithographic techniques, down to lab-on-a-chip devices hosting electrochemical cells [60]. In addition, the development of proper flow cells reached a mature stage [61, 62]. Micromechanical engineering also allowed flow cells to become continuous-flow microfluidic cells. Miniaturisation and automation in the production of devices were also the basis for the commercial availability of disposable,

screen-printed electrochemical cells. They permit one to exploit those electrode systems that are poorly stable over time and make them suitable for a number of *in vivo* applications.

Few additional real innovations on the instrumentation have emerged in recent years. They are potentially of high impact in the field of amperometric sensing but, at the moment, are confined in niches. This is, for instance, the case of enhancing the mass transport and reducing the fouling of the electrode surface through the use of ultrasounds, microwaves, light and heat [63, 64]. The coupling of optical techniques with electrochemical ones for analytical purposes is still under investigation; different approaches have been proposed, including electrogenerated chemiluminescence [10] and the contemporary and independent acquisition of electrochemical and optical signals [65, 66]. Finally, hyphenated technique based on mass spectrometry has been recently proposed [61].

As evidenced for the previous decades, electroanalysis poorly exploited a number of novel functional conducting materials also in the recent years. This criticism constitutes, to our opinion, a key point, and it is a sound Leitmotiv along these pages. As reported previously, the electrode systems realised belong to different classes of materials, so that a proper classification is particularly difficult. Only the most important ones are described hereafter; in particular, the discussion is focussed on conducting polymers (CPs), SAMs and nanostructures. Other electrode modifiers, including most of those described in the previous section, are still studied, but their relative weight within the scientific literature is decreasing in recent years. As a general consideration, a part of the success of the new electroanalytical approaches is actually due to the development of other branches of electrochemistry, such as fuel cells and electrodeposition. Furthermore, it is noteworthy that a very important favourable element lies in the easier and easier availability, on the market, of chemicals that once required to be synthesised on purpose and were hence *a fortiori* very difficult to propose for more or less routine analyses. At the same time, a number of different analytes have been quantified by means of these materials, high enough to render a list of them poorly compatible with the aim of the present article.

CPs represent one of the most popular classes of materials, definitely not limitedly to electrochemistry [67]. In particular, CPs based on thiophene, pyrrole and aniline have been most intensively studied, the research on thiophene-based materials being also triggered by their use in organic electronics, *i. e.* a novel branch of semiconductor science [68]. On the one hand, the already cited commercial availability of suitable monomers strongly facilitates the wide diffusion of these materials but, on the other hand, the possibility to functionalise their structure in a relatively easy way has led to a number of different polymers possessing peculiar properties.

Actually, a number of alternative monomers can be, in principle, employed in electroanalytical applications [69, 70], and a consequent even wider number of co-polymers may be correspondingly taken into account. CPs have been deposited mainly through direct electrogeneration on the electrode surface, although other methods, such as LbL deposition, have been proposed [67, 71]. Successful electroanalytical applications have been reported [72, 73]. However, the establishment of a clear relationship between the electroanalytical performances and the characteristics of the polymers is often rather difficult, also because many intrinsic properties of the polymeric coatings, such as the semi-crystalline structure, the polydispersion of the backbone, the corrugated morphology and the insolubility, prevent from performing an exhaustive characterisation. In addition, the definition of the charge transfer mechanism of the analyte on the polymer surface is often much more difficult than on planar metal surfaces, being complicated by different reciprocal interactions. As a consequence, it is hard to estimate in advance the influence of the nature of the polymer and of the preparation procedure on the electroanalytical performance.

After the seed works reported in the previous section, SAMs have been deeply investigated in recent years. The most efforts have been devoted to anchoring thiol-based molecules on metal substrates, in particular on Au. However, a number of different molecules and substrates have been proposed [74]. In many cases, SAMs possess a high degree of molecular order that facilitates the investigation of the structure. The studies have even allowed an atomistic description of the systems, also thanks to surface science investigation in ultra-high vacuum condition, carried out in the frame of other branches of science [75].

The term SAM has been extended also to systems possessing a poor degree of order and a thickness often exceeding that of a monomolecular layer. As an example, thin films built up starting from diazonium salts [76] are often based on oligomeric, disordered molecules grafted on the substrate. Similarly to the case of CPs, the commercial availability of SAM precursors and the relatively easy synthesis of novel molecules encourage a large number of studies. In addition, the preparation procedures of similar electrode systems are quite straightforward, often involving the simple dipping of the substrate in a dilute solution of the precursors. The main limitation to the use of most SAM-based systems in electroanalytical applications, especially in real matrices, seems to be due to their poor chemical and thermal stability. However, the recent widespread diffusion of disposable devices, thanks to the preparation procedures cited, ascribes SAM's new, increasing importance.

The development of *nano-objects* constitutes one of the most active research fields in recent years. Incidentally, it should be evidenced that the term *nano-object* is often

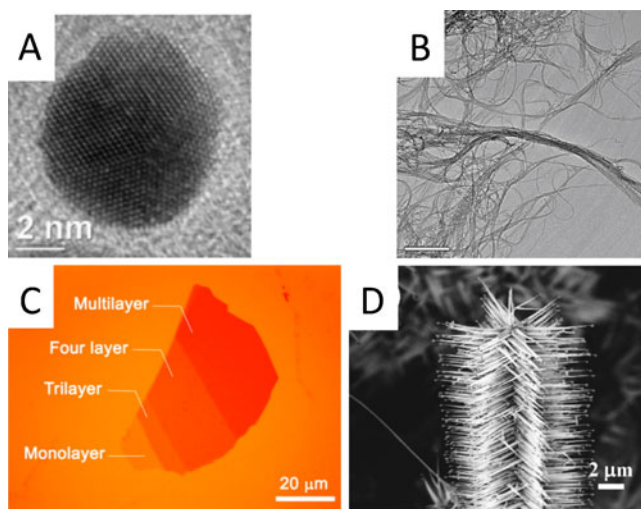
improperly used in the literature to indicate micro-objects. It is worth recalling that only materials possessing at least one dimension down to a certain threshold (typically 20 nm) exhibit peculiar properties that are different from those of the corresponding bulk material, even when finely divided. Hence, the fashion of materials under “nano” forms is often not really a fashion in such fields as electroanalysis. The peculiar properties of true nanostructured materials, e.g. the electrocatalytic activity of metal nanoparticles, cannot be observed in the case of finely divided metal microparticles [77].

0D, 1D, 2D and 3D nano-objects (Fig. 2) have been fabricated using both bottom-up and top-down approaches [78–82]. The former ones are based on the chemical transformation of molecular precursors into nano-objects, while the latter ones imply the fragmentation of a bulk material into the corresponding nano-objects. The composition of these can be varied over a very wide range. Literature reports the formation of nano-objects based on almost all elements of the periodic table, as well as on organic polymers [83]. In addition, the preparation of chalcogenides, carbides and nitrides, even of complex chemical composition, is rather popular [84, 85]. In most cases, electroanalytical applications have been so far developed employing metal nanoparticles; noble metals, such as Au and Pt, are the most popular ones [86]. However, the research is also evolving toward the use of multicomponent metal systems, not necessarily based on proper alloys [87]. The peculiar synergistic effects exhibited by multicomponent systems enhance the analytical performances. Moreover, the use of nano-objects different from nanoparticles is more and more popular [88]. It is worth noticing that the research in the field

has been triggered also by the astonishing results obtained in the development of the electrocatalysts for low-temperature fuel cells [85]. A second class of nano-objects, also employed in electroanalysis, is based on C. In particular, single- and multi-wall C nanotubes have been widely employed, also thanks to the commercial availability and to the development of effective protocols for their purification and functionalisation [89]. More recently, diamond-based nanomaterials [63, 90] and graphene [91–93] have been investigated as electrode modifiers; however, the single-layer nature of the graphene deposit formed is questionable. Surprisingly enough, research efforts directed to electroanalytical applications of nanostructures based on such materials as metal oxides are very limited, also owing to the low number of studies on the corresponding bulk materials [93]. Actually, similar materials often possess a poorly defined stoichiometric composition at the outermost surface, which is reflected, definitely enhanced, in the situation of the relevant nano-objects. Recently, the coupling of metal or C nanostructures with oxide-based materials has been reported [89].

Nanostructures can be prepared and anchored directly on the electrode surfaces. The electrodeposition of metal nanostructures constitutes a typical example, the procedures being largely borrowed from the scientific and industrial studies on electrodeposited coatings [94]. A part of the research dealing with the nanostructures has been devoted to develop more or less ordered nanostructured electrode surfaces by means of physical and chemical methods, in particular based on lithography [95]. In addition, a significant fraction of the studies uses suitable binders in order to stably anchor nano-objects. Different approaches have been followed, such as the formation of SAMs or the use of polymeric materials: the use of polymers constitutes the most popular method, leading to the formation of nanocomposites [63, 89–96]. Among the polymers, CPs have represented the most spontaneous approach [63, 72–77, 82–97], although the use of a non-conductive polymeric matrix, including conductive nanostructures well above the conduction threshold concentration limit, has been employed. As an example, a number of metal and C-based nanoparticles have been dispersed in chitosan for the determination of different species [98]. Different deposition procedures have been adopted, e.g. drop casting, spin coating, electrodeposition and LbL deposition [97]. In addition, carbon-paste composites are still proposed for electroanalytical applications [90–99].

Part of the recent efforts in the development of electroanalysis has been triggered by the use of biomaterials [100, 101]. Once more, it is rather difficult to classify the large number of different biomolecules and analytical strategies adopted so far. Many successful



**Fig. 2** Examples of 0D, 1D, 2D and 3D nanostructures: Au nanoparticle (a, [78]), bundles of carbon nanotubes (b, [79]), single layer of graphene (c, [80]) and ZnO nanopropeller (d, [81]). Images have been reprinted with permission



procedures have been proposed, leading to amazing low detection limits and high selectivity. The miniaturisation of these sensing systems allows the use of tiny amounts of solution, which constitutes a crucial aspect for the development of commercial products. Most of them take advantage of the different electrode modifiers previously described: they guarantee stable anchoring of the biomaterials and effective electron transfer to the underlying electrode. As an example, the anchoring of many proteins has been achieved thanks to the chemical reactions with the surface of properly designed SAMs. Actually, amperometric biosensors suffer from some limitations: in particular, the stability of the electrode modifiers is rather poor, from both the chemical and thermal point of view. A criticism already made on many occasions in these pages should be repeated once more. Though most research efforts in biosensing have been addressed to issues of importance in clinical and environmental analytical chemistry, the modified electrodes have been, however, employed basically in the investigation of “simple” laboratory-prepared solution. Real matrices, or even synthetic ones prepared to mimic them, are still poorly investigated.

### Chemometrics applied to electroanalysis

Aiming at discriminating and classifying categories of (real) complex matrices similar to one another, though different as to one or more specific aspects, what is often called “blind analysis” has diffused for decades, based on spectroscopic techniques, especially in the NIR region. Multivariate regression techniques have also been successfully applied to evaluate single specific parameters of importance, on the basis of signals that are in no way interpreted in the frame of compositional analysis. In addition to mass spectrometers, non-specific sensing systems for vapours (*electronic* or *artificial noses*) [102] have been already on the market for almost two decades. They are for the most part based on conductivity variations of semiconducting elements.

Similar systems for liquid matrices, also called *electronic* or *artificial tongues*, have been more recently developed, based on potentiometric or amperometric techniques. Although some devices are already commercially available, much research should be made in order to achieve fully satisfactory performances [103].

These sensing systems deserve a specific discussion. First of all, it should be recalled that they are not required to give selective responses, i.e. capable to discriminate among different substances, but only to be “partially selective”. The relevant responses are required to bear suitable information content to allow grouping of samples of the same category and discrimination among different categories. It should be also emphasised that analytical chemists

are often still poorly familiar with blind analysis, so much so that the researchers in the field often constitute a self-standing “ethnic” group, often close to be considered something odd, even not always completely believable. Maybe, the approach to blind analysis is even harder for electrochemists, who are faithful of the fact that  $(1+1)/2=1$ , rather than a number varying between 0 and 2, 1 being (often) only the most probable value. Engineers are more involved in these fields, which clearly opens the doors to complementary scientific expertise.

Noteworthy, relatively recently, the blind analysis approach has been encouraged by the US Food and Drug Administration (FDA), since it facilitates faster, cheaper and more reliable management for industrial processing, optimisation and control. According to FDA, measurements collected from sensors need not to be absolute values of the attribute of interest. The whole concept introduced and promoted by FDA is called Process Analytical Technology and is of high relevance to pharmaceutical and food industries [104–106]. It is important to notice that little efforts were made till few years ago in testing unconventional materials for amperometric non-selective sensing systems, as well as in paying attention to the selectivity of each class of matrices with respect to the physical device proposed. These are sound reasons why amperometric sensing is expected to devote much more care to similar systems in the next future. The content of useful information brought by a voltammetric response can take greatest advantage from electrode materials difficult to foul and activating electrocatalytic processes that induce deconvolution of overlapped signals. In such a context, reproducibility of the electrode systems constitutes a further urgent request, in order to use repeatedly the chemometric model built, also considering the high probability to be forced to use disposable cells. Finally, electroanalysts developing and testing similar systems should be well aware of the chemometric issues that are involved in an effective proposed global system. The lack of such a consciousness has been too often the cause of bad functioning and consequent distrust with respect to blind sensing.

**Acknowledgements** Gino Bontempelli, Franco Magno, and Gian-Antonio Mazzocchin are thanked by R.S. for making him start the adventure in Padova. Laura Pigani and Chiara Zanardi are thanked by both of us for going on the adventure in Modena.

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