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Composite silica-based films as platforms for electrochemical sensors

Oksana TANANAIKO,^{1,*} Alain WALCARIUS^{2,*}

¹ *Department of Analytical Chemistry, National Taras Shevchenko University of Kyiv,
Volodymyrska Str., 64, Kyiv, Ukraine, 01601*

² *Université de Lorraine, CNRS, LCPME, 54000 Nancy, France*

* *Corresponding authors: otananaiko@gmail.com (Tel.: +380 (44) 239 34 44;
+380 (67) 892 34 82), alain.walcarius@univ-lorraine.fr (Tel.: +33 (3) 72 74 73 75)*

Abstract

Sol-gel-derived silica thin films generated onto electrode surfaces in the form of organic-inorganic hybrid coatings or other composite layers have found tremendous interest for being used as platforms for the development of electrochemical sensors and biosensors. After a brief description of the strategies applied to prepare such materials, and their interest as electrode modifier, this review will summarize the major advances made so far with composite silica-based films in electroanalysis. It will primarily focus on electrochemical sensors involving both non-ordered composite films and vertically oriented mesoporous membranes, the biosensors exploiting the concept of sol-gel bioencapsulation on electrode, the spectroelectrochemical sensors, and some others.

Key words: thin films, sol-gel materials, composites, mesoporous silica, modified electrodes, electrodeposition, sensors, biosensors.

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1 **1. Introduction**

2 The progress in the development of affordable and reliable methods for the analysis
3 of the complex objects or real media, while avoiding the need for time consuming sampling
4 procedures or expensive apparatus, requires special attention to chemical and biochemical
5 sensors. The development of sensors is accompanied by the synthesis of recognition
6 elements on the surface of transducers for sensitive and selective detection of the target
7 analyte. They must possess a long-term stability, satisfactory reproducibility and sensitivity
8 of the analytical signal. Significant advances in chemical/biochemical sensors have
9 occurred in recent two decades due to the ever-growing emergence of various kinds of thin
10 films that can be engineered onto transducer surfaces, especially electrodes.^[1, 2] A particular
11 attention is paid to composite films in which the dimension of the layer ranges between few
12 nanometers to micrometers. They are built by mixing two or more dissimilar components
13 and, as a result, a new material with improved properties and structure is formed. The
14 properties of the composite films depend not only on the individual components used but
15 also on the morphology and the interfacial characteristics.^[3] When two or more constituents
16 are combined, the properties of a traditional coating can be refined to address specific
17 requirements.^[4] Composite films associating distinct materials are likely to provide
18 synergetic or complementary behaviours. This may lead to unique physical, chemical,
19 optical, mechanical, magnetic or electrical properties that are unavailable or less marked
20 from just one component. Such multicomponent materials have attracted more attention as
21 sensitive elements of electrochemical sensors. Various composites are examined for the
22 construction of the recognition elements of many electrochemical sensors, including organic
23 and inorganic polymers, as well as macromolecules mixed or doped with metals or metal
24 oxide (nano)particles and (or) with carbon nanomaterials.^[3, 4, 5] The precise attention is paid
25 to polymeric materials combined with biomolecules and nanoparticles of different nature.^{[1,}

1 ^{2, 6]} Among them, thin films based on silica and sol-gel materials are of big interest, notably
2 because they can be easily combined and (or) functionalized with different kind of organic
3 and inorganic substances.

4 In spite of its insulating nature and although not redox-active, silica has found
5 interest in electrochemistry in general and in electroanalytical chemistry in particular. Major
6 advances made during the last century have been largely reviewed.^[7-11] At that time, the
7 investigations were mainly based of bulky silica-based materials (most often as powders
8 dispersed into a conductive matrix such as carbon paste electrodes) or deposited as thick
9 films (most often with a polymeric binder to maintain the silica particles more durably onto
10 the electrode surface). In the past two decades, more and more works have been devoted to
11 the exploitation of thin layers made of a continuous silica film uniformly deposited onto a
12 solid electrode support, thanks to the versatility of the sol-gel process,^[11-14] including those
13 exhibiting an ordered structure at the nanoscale.^[14-16] These materials are attractive as they
14 bring additional properties compared to the traditional electrochemical interfaces, such as
15 their ability to recognize target analytes (enabling their accumulation prior to detection),
16 their host properties for various biocatalysts and/or electrocatalysts, their permselective
17 behaviour, or their ability to ensure fast mass transport of guest species (as a result of their
18 rigid three-dimensional framework).^[14, 17] They can be easily manufactured in the form of
19 organic-inorganic hybrids or as nanocomposite materials by implementing the numerous
20 possibilities offered by the sol-gel process.^[17-20] Silica-based organic-inorganic
21 nanocomposites have a long history and are usually classified into two categories depending
22 on whether the organic and inorganic components are interacting via weak bonds (class I)
23 or are linked by covalent or iono-covalent chemical bonds (class II).^[21] The interest of the
24 first category relies on the ability to entrap redox proteins or enzymes, nanocarbons or metal
25 nanoparticles catalysts, electrochemiluminescence reagents, or electroactive polymers,

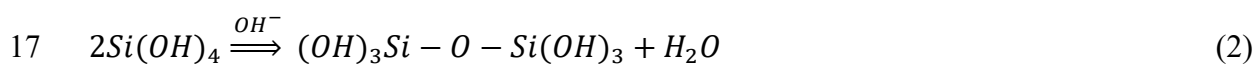
1 which remain accessible to external reagents or target analytes owing to the rigid three-
2 dimensional and porous inorganic network.^[14, 16, 20, 22] This is essential for the proper
3 functioning of electrochemical sensors and biosensors. The second category is also very
4 attractive in this field as the rich chemistry of organosilane reagents enables the covalent
5 bonding of various organo-functional groups that can be exploited for the selective
6 preconcentration and/or electrocatalytic sensing of target species, or for the attachment of
7 suitable mediators necessary in electrochemical biosensors, for instance. From that point of
8 view, the advent of the ordered mesoporous silica materials (that can be also prepared in
9 thin film configuration^[23]) has opened new avenues. They enable very fast molecular
10 transport (leading to enhanced electrochemical signals^[24]), they can be functionalized by a
11 large number of organo-functional groups that remain highly accessible owing to the regular
12 and widely open porous structure, making them particularly interesting in electrochemistry
13 and sensing.^[16, 25] Moreover, combining the sol-gel process with interfacial surfactant
14 templating allows a preferential vertical orientation of the nanochannels with respect to the
15 underlying electrode support, including in a chemically modified form,^[26] being especially
16 promising for analytical purposes.^[27]

17 In this review, we will cover the main advances made in the past two decades in
18 the development of electrochemical sensors and biosensors manufactured from continuous
19 sol-gel-derived silica-based composite (or doped) thin films. We will first describe briefly
20 the strategies applied to generate these composite layers onto solid electrode surfaces and
21 then discuss their use in designing electrochemical sensors and biosensors made of
22 composite and/or biocomposite films integrating silica along with molecular reagents,
23 biomolecules, organo-functional groups, polymers, surfactants, molecular imprints,
24 inorganic nanoparticles or other nanomaterials.

25

1 2. Strategies for confining silica-based materials to electrode 2 surfaces

3 Silica is an electronic insulator and its use in electrochemistry requires the
4 establishment of a close contact to an electrically conducting material. A straightforward
5 way is to disperse silica-based nanoparticles in carbon paste electrodes or in the carbon ink
6 used to fabricate screen-printed electrodes,^[10] or to deposit them onto a solid electrode
7 surface usually together with a polymer binder to ensure the mechanical strength of the
8 resulting composite, as for other inorganic particles-based thick films.^[28] In order to avoid
9 unwanted matrix effects, the above approaches were rapidly supplanted by strategies
10 directed to the one-step generation of continuous silica-based thin films onto electrode
11 surfaces by exploiting the versatility of the sol-gel process.^[11-16, 29] The main deposition
12 procedures are illustrated in Figure 1A. A sol solution is prepared from silica precursors
13 (*i.e.*, tetraalkoxysilane species, Si(OR)₄, usually in hydro-alcoholic medium) that are
14 hydrolyzed (Eq. 1) to form a stable sol, the aging of which being likely to induce the
15 formation of a gel upon condensation (Eq. 2) in the presence of a suitable catalyst.^[30]



18 For film preparation, the polycondensation of the hydrolyzed precursors is usually induced
19 by solvent evaporation (thus concentrating the silica precursors and favouring therefore
20 their condensation without the need for a catalyst). This can basically be achieved by
21 dropping an aliquot of the sol solution onto a solid surface and letting it evaporate, but more
22 controlled methods are dip-coating or spin-coating where the sol-gel film is obtained by
23 gravitational or centrifugal draining associated to fast drying.^[31] In doing so, one can tailor
24 the deposition process to form thin films of different thickness and structure by varying the

1 sol composition (especially the precursors' concentration) and controlling the evaporation
2 rate. The film gel is then dried/cured to complete the formation of the silica network. Such
3 coating can be formed on any type of flat supports, including electrode surfaces and in multi-
4 layer configurations.^[29] An alternative in sol-gel thin-film design on electrode is via an
5 indirect electrodeposition method.^[32, 33] In this case, a pH increase is induced at the
6 electrode/solution interface by applying a suitable negative potential to the electrode
7 (reducing water into OH⁻ species), acting as a catalyst for the condensation of the silica
8 precursors. Again, the film thickness can be controlled by adjusting the synthesis conditions
9 (sol composition, applied potential and duration of the electrodeposition). An advantage of
10 the electrodeposition method over the evaporation-based ones is the possibility of getting
11 uniform deposits on electrodes with complex geometries such as macroporous metals,^[34]
12 metal nanofibers,^[35] or carbon micro- and nanomaterials.^[36, 37]

13 The above dip-coating, spin-coating and electrodeposition methods can be easily
14 extended to the production of silica-based composite thin films, as illustrated in Figure 1B.
15 At first, the addition of an organo-trialkoxysilane (R'-Si(OR)₃, with R' being a selected
16 organo-functional group) into the starting sol leads to its co-condensation with Si(OR)₄ and
17 the formation of an organic-inorganic hybrid network of organo-silica bearing the organic
18 functions R' attached in a covalent way to the inorganic structure (see part (a) in Fig. 1B).
19 The amount of incorporated organic groups can be tuned by varying the R'-Si(OR)₃/Si(OR)₄
20 molar ratio in the precursors solution, and multi-functionalized composite films can be
21 obtained by adding one or more R'-Si(OR)₃ reagents in the medium.^[17-20] Electrodeposition
22 can be also implemented to generate such organically-modified deposits.^[38] Other types of
23 composite layers are obtained by exploiting the hosting properties of porous silica, and
24 especially the versatility of the sol-gel process to enable the direct entrapment of
25 biomolecules, nano-objects or even polymeric materials in the course of film formation, by

1 simply dispersing these additives in the starting sol solution (see illustrations in part (b) of
2 Fig. 1B). As a matter of fact, thanks to the room temperature processing of the method, sol-
3 gel bioencapsulation is becoming an elegant way to confine biomolecules in a rigid three-
4 dimensional matrix while keeping their biological activity,^[39] including as thin films onto
5 an electrode surfaces for applications in the biosensors field.^[7, 22] Silica-based biocomposite
6 thin films can be also produced electrochemically, as pioneered for redox proteins
7 bioencapsulation by two independent groups in 2007,^[40, 41] and later on also for much bigger
8 biological agents such as bacteria, leading to artificial biofilms.^[42] Otherwise, several other
9 nano-objects have been entrapped into silica films during their sol-gel processing. With
10 respect to their attractiveness for the development of electrochemical sensors, they
11 encompass primarily noble metal or metal oxide nanoparticles and carbon particles, giving
12 birth respectively to metal- and carbon-ceramic composite electrodes,^[9, 20, 43] which can be
13 also prepared as thin films but mainly by electrochemically assisted deposition (EAD).<sup>[44-
14 48]</sup> These modifiers are exploited in particular for their electrocatalytic properties and/or as
15 an effective means of imparting electrical conductivity to the silica-based composite layer.
16 Co-encapsulation of biomolecules and metal nanoparticles or carbon nanomaterials is also
17 documented for bioelectrocatalytic sensing.^[49, 50] Finally, interpenetrated organic polymer-
18 silica composite films can be produced by either polymer doping or polymer grafting during
19 sol-gel deposition, as well as polymerization of organic polymers within pre-formed silicate
20 films,^[14, 43] or indirectly electrodeposited via interfacial pH change by EAD.^[51] Combining
21 electropolymerization and sol-gel electrodeposition is also possible, leading to the
22 formation of conductive polymer-silica hybrid thin films.^[52]

23 Of particular interest are the regularly ordered and widely open silica
24 mesostructures that are formed by the template route because they offer incomparable
25 permeation properties when deposited as thin films on electrodes,^[24, 53-55] and better

1 accessibility to the active sites when prepared in the form of organic-inorganic hybrids as
2 compared to their non-organized analogs,^[56, 57] which is of outstanding importance in the
3 development of electrochemical sensors.^[16] They are usually prepared by evaporation
4 induced self-assembly (EISA) from a sol solution containing the silica precursors and
5 surfactant molecules, which is deposited onto a solid support by dip-coating, leading to the
6 self-assembly of silica-surfactant micelles upon evaporation and their deposition as
7 lyotropic liquid crystalline mesophases onto the support surface.^[58, 59] EISA is a versatile
8 and controllable soft-templating method to prepare mesoporous thin films, but it suffers
9 from some limitations when attempting to control the alignment of the mesochannels with
10 respect to the underlying support (especially in a vertical orientation), which requires
11 alternative approaches.^[23] And this is important as a vertical orientation of mesopores
12 should be the best configuration to ensure fast transport through the membrane for
13 reagents/analytes to reach the electrode surface, promoting high sensitivity for
14 electrochemical detection.^[27] The two main methods likely to reach this goal, and applied
15 so far to manufacture electrochemical sensors, are presented in Figure 2. The first one is the
16 so-called electrochemically assisted self-assembly (EASA) discovered in 2007,^[26, 60, 61]
17 involving an electrochemically induced vertical growth of silica walls around cationic
18 surfactant hemi-micelles concomitantly formed on the electrode surface biased at a suitable
19 negative potential (see part (a) in Fig. 2A). Such a combination of electrochemical
20 interfacial surfactant templating and electrochemical modulation of the sol-gel process
21 constitutes an easy, fast (few seconds) and versatile way to get highly ordered mesoporous
22 silica films made of a hexagonal packing of mesopores (see part (b₁) in Fig. 2A) with vertical
23 orientation (see part (b₂) in Fig. 2A), as also confirmed by grazing-incidence X-ray
24 diffraction (see part (c) in Fig. 2A). The obtained films cover uniformly the electrode surface
25 with typical thicknesses around 80 nm (see part (d) in Fig. 2A) and they can be prepared in

1 multilayer configuration while maintaining the mesopore interconnection between each
2 layer (see part (e) in Fig. 2A). Thicker films (μm scale) can be obtained by using an
3 alternative current-assisted deposition method.^[62] They can be functionalized with a variety
4 of organo-functional groups by combining the EASA method with click chemistry,^[63, 64]
5 and if attaching redox-active groups to the mesopore walls (such as ferrocene as illustrated
6 in part (f) of Fig. 2A), they remain electrochemically accessible in spite of the insulating
7 nature of the silica membrane thanks to effective electron hopping between adjacent
8 ferrocene moieties.^[65] They can also serve to grow conducting polymer nanofilaments or to
9 immobilize other redox-active components.^[26] The second approach is the Stöber solution
10 growth method (Fig. 2B) proposed in 2012.^[66] The growth mechanism involves a gradual
11 transformation of silicate–cationic surfactant composites from spherical to cylindrical
12 micelles with the assistance of ammonia hydrogen bonding and controlled silica
13 condensation (see part (a) in Fig. 2B). The driving force is the slow hydrolysis (hour scale)
14 of tetraethoxysilane (TEOS) molecules in an ammonia and ethanol solution, at a
15 concentration low enough to enable their preferential deposition at the junction between the
16 spherical micelles and the substrate, favouring the formation of parallel mesochannels
17 growing perpendicularly to the substrate in the form of films with uniform thickness (see
18 parts (b) and (c) in Fig. 2B) and a high level of ordering (see parts (d) and (e) in Fig. 2B).
19 The method is basically applied to deposition only onto hydrophilic substrates but also onto
20 pre-formed mesoporous supports as porous alumina.^[67] The films can be detached from the
21 surface and, thanks to the monodisperse diameter of mesochannels at few nanometres, the
22 resulting free-standing membranes can be applied to molecular separation, for instance.^[68]
23 For both methods (EASA and Stöber growth), the film porosity is revealed by removing the
24 surfactant template by solvent extraction or calcination, the latter being evidently restricted
25 to non-functionalized materials. These films are characterized by both charge and size

1 selectivities at the molecular level,^[69, 70] making them unique permselective membranes on
2 electrode surfaces.^[26, 27]

3

4 **3. Electrochemical sensors designed from composite silica films**

5 Hereafter, we will distinguish the electrochemical sensors made of non-ordered
6 silica materials (*i.e.*, ‘classical’ sol-gel-derived silica-based composites) in section 3.1,
7 while considering the specific case of ordered silica films (*i.e.*, as obtained using surfactant
8 templates) in section 3.2.

9 **3.1. Composite films based on non-ordered silica**

10 Non-ordered silica films are widely used in electrochemistry as electrode modifiers
11 in spite of their insulating properties.^[8, 10, 14] To improve their ionic or electronic
12 conductivity, organic or inorganic conductive/electroactive additives or nanomaterials are
13 often used in the construction of silica-based electrochemical sensors.^[71-75] The open
14 structure of silica films ensures proper access of the analyte to the functional groups at the
15 electrode/film/solution interphase and makes possible an effective accumulation of trace
16 amounts of the analyte, which contributes to enhanced sensitivity of the determination. The
17 selection of appropriate analytical reagents or functional groups attached to – or
18 encapsulated in – silica films can lead to selective extraction and preconcentration of the
19 target analyte from complex mixtures on the surface of such modified electrodes. The
20 incorporation of redox-active species such as charge transfer mediators into the silica matrix
21 allows to increase significantly both sensitivity and selectivity of the sensors due to their
22 electrocatalytic properties helping at improving the determination of the target analytes.<sup>[76-
23 ^{80]} A great diversity of modification has opened wide prospects for obtaining sensitive</sup>

1 elements of electrochemical sensors based on sol-gel modified electrodes in recent decades.
2 Sol-gel-derived silica films are prepared on electrode surfaces as specified in Section 2, and
3 most of the obtained sensors^[71-82] are operating in voltammetry, amperometry,
4 electrochemiluminescence or electrochemical impedance spectroscopy, in static conditions
5 or in flow analysis modes.^[79] The various types of electrochemical sensors based on non-
6 ordered silica composite films are presented hereafter, depending on whether they consist
7 of silica films comprising polyelectrolytes or organic reagents, silica-nanomaterials
8 composites, or silica-based molecularly imprinted polymers (MIPs). The analytical
9 characteristics of the two first categories are presented in Table 1 whereas the data relative
10 to MIPs-based sensors are gathered in Table 2.

11 *3.1.1. Non-ordered silica films containing polyelectrolytes and organic reagents*

12 The incorporation of organic polyelectrolytes in silica-modified electrodes may
13 contribute to improve their conductivity (*i.e.*, for conducting polymers) or to accumulate
14 analytes or reject interferences via electrostatic interactions (*i.e.*, for charged polymers),
15 with possible enhancement of selectivity and sensitivity for the developed sensors. For
16 example, trace amounts of Mo(VI) in vitamins was achieved using a pyrolytic graphite
17 electrode modified with a SiO₂-polydimethyldiallylammonium chloride film and an anionic
18 azo dye lumogalion adsorbed on the film surface.^[75] The best conductivity and mass transfer
19 properties were exhibited by the composite film obtained in the presence of non-ionic
20 surfactant Tween 20. The electrode can be regenerated and reused for 5 times. Improved
21 stability was also reported when using a Nafion layer over a functionalized silica film
22 applied to the detection of heavy metal ions.^[71] Poly(vitamin B1) electropolymerized onto
23 a nanocomposite silica (SBA-15) incorporating V₂O₅ and CeO₂ contributed to enhance both

1 the conductivity and the stability of the modified electrode applied to the determination of
2 nitrophenol derivatives in the environment, demonstrating a lifetime as long as 30 days.^[81]

3 Organic reagents can be also accommodated to silica films either by soft binding
4 (adsorption) or by covalent attachment, this latter approach leading generally to more
5 durable immobilization. Anionic redox mediators (hexacyanoferrate) were immobilized by
6 electrostatic interaction on protonated amine-functionalized silica film on a gold electrode,
7 and demonstrated good stability when applied to the determination of nitrite ions in water
8 by flow injection analysis.^[82] Another example is the determination of ascorbic acid in
9 human plasma using a composite material made of manganese porphyrin mediator
10 entrapped in a silica film generated on carbon electrode by the laser ablation deposition
11 technique.^[72] Voltammetric sensors for Cd^{2+} , Pb^{2+} and Cu^{2+} , were developed by coating
12 glassy carbon electrodes with a composite of thiol self-assembled monolayers on
13 mesoporous silica supports (to accumulate the metal ions) and Nafion layer (to enhance
14 plasticity). They enabled detecting 0.5 ppb of Pb^{2+} and 2.5 ppb of Cd^{2+} in river water,
15 groundwater, and seawater with a minimum preconcentration.^[71]

16 *3.1.2. Non-ordered silica films and nanomaterials*

17 As reported in Table 1, several nano-objects can be used as additives in silica films
18 on electrodes, such as metal nanoparticles, carbon nanomaterials, or metal oxides.

19 Metal nanoparticles, especially those based on noble metals, are attractive modifiers
20 of silica films because they enable considerable improvement of their conductivity and
21 electrocatalytic properties.^[83, 84] They contribute to increase the sensitivity and selectivity
22 of silica-based electrochemical sensors due to enhancing the electroactive surface area of
23 the modified electrodes and electron mediating properties between the analyte and the
24 electrode surface. Examples are available for silica films bearing nanoparticles of gold

1 (AuNP),^[76, 79, 85, 86] silver (AgNP),^[80, 87] or lead (PbNP).^[88] Most often, organically modified
2 silica (ORMOSIL) is used as the host matrix with chelating groups that are likely to stabilize
3 durably the metal nanoparticles on the electrode surface.^[76, 79, 80, 86, 88] AgNP demonstrated
4 electrocatalytic activity towards nitrite ions,^[80] and enabled selective cyanide sensing in
5 electroplating wastewater samples.^[87] The presence of PbNP improved the response of a
6 thiol-functionalized silica film electrode for ultrasensitive silver sensing, reaching a
7 detection limit down to 1.2 pM of Ag(I) after 90 s of accumulation.^[88] AuNPs were most
8 often exploited for their electrocatalytic properties (*e.g.*, for H₂O₂ detection^[85]), sometimes
9 associated in a synergetic way to other species (*e.g.*, mediators), as exemplified for a glassy
10 carbon electrode modified with a mesoporous silica film containing rhodium(II)
11 phosphomolybdate and AuNPs as sensitive element of a flow amperometric sensor for
12 bromate ion and methionine.^[79] The electrode demonstrated stable response in flow-
13 injection amperometric mode for more than 100 measurements per day.

14 Carbon-based nanomaterials can also help at increasing the electronic conductivity
15 of the film and improving its electrocatalytic features, as pointed out for single and multi-
16 walled carbon nanotubes,^[78, 89] graphene oxides,^[76, 86, 90] or other nano-carbons.^[73] They
17 were mostly exploited for the determination of biologically relevant molecules such as
18 dopamine, acetaminophen (paracetamol) or uric acid (Table 1), sometimes associated to
19 metal nanoparticles (AuNP) or metal oxides (Fe₂O₃).^[73, 86] A particular family is that of
20 humidity sensors based on impedance or resistance measurements that are proportional to
21 air humidity. This is the case of mesoporous silica-carbon nanotubes composites,^[89] or
22 mixed silica-titanium composite film obtained from titanium(IV) n-butoxide and
23 polydimethylsiloxane deposited in the presence of a Ce-dopant onto silver palladium planar
24 electrodes,^[91] to name but a few.

1 3.1.3. Molecularly imprinted silica-based films

2 The development of silica films with imprinted target analyte is a prospective way
3 to obtain a new type of highly specific molecularly imprinted polymer (MIP) mimicking the
4 molecular recognition of organic molecules by biological molecules.^[92-95] Such films called
5 “molecularly imprinted silica” (MIS) are widely used as sensitive elements of
6 electrochemical sensors (Table 2). Typical MIPs can be obtained by polymerization
7 involving either non-covalent imprinting (which can be realised by physical, hydrophobic,
8 van der Waals forces, hydrogen bond or electrostatic interactions between the analyte
9 molecule and the polymer network) or imprinting via reversible covalent attachment.^[92] For
10 MIS materials, the most common strategies include non-covalent entrapment.^[96] MIS films
11 are fabricated using the sol-gel technique and the overall procedure involves successive
12 steps: (1) the preparation of a sol containing the suitable silica and organosilica precursors
13 and the target probe molecule (called “template”), (2) the physical entrapment of the
14 template during gelation (cross-linking) of the sol, and (3) the removal of the template from
15 the dry silica matrix. The functionalized organosilica precursors (*i.e.*, mainly phenyl-,
16 methyl- or vinyl-trialkoxysilane reagents, but also aminopropyltriethoxysilane) are selected
17 for their possible interactions with the target molecule, whereas the tetraalkoxysilane acts
18 as network former, to get the final ORMOSIL. The template molecules are generally small
19 and have a rigid planar structure, which is important for leaving clear imprints in the silica
20 matrix. After synthesis, the template molecule is removed from the porous MIS film via
21 soaking in aqueous buffer or organic solvent. Various routes for coating MIS onto electrode
22 surfaces can be followed (Fig. 3A).^[96] The most straightforward ones are based on the
23 physical deposition of the sol by spin-coating or drop casting, for which gelation is induced
24 by evaporation with concomitant MIS formation.^[97-100] They are convenient for film
25 formation on flat electrode supports. Sometimes, they are combined with strategies to ensure

1 durable chemical attachment of the MIS to the electrode, which implies the use of an
2 organosilane acting as a molecular glue between the silica film and the electrode surface.<sup>[101-
3 103]</sup> Electro-assisted deposition (EAD) is also a powerful mean to generate MIS films of
4 controlled thickness,^[74] and is particularly suited to the preparation of uniform MIS deposits
5 on heterogeneous electrode surfaces (*i.e.*, made of carbon nanotubes assemblies of graphene
6 oxide layers).^[104-107]

7 MIS films can offer several advantages compared to organic polymer-based MIP
8 materials. Silica films are easy to obtain by the sol-gel process, quite rapidly and at room
9 temperature, avoiding any thermal or chemical decomposition of the imprinted molecules.
10 They are mechanically stable due to their three-dimensional rigid structure made of a high
11 level of cross-linking, which is also favourable to a rather fast mass transport of the target
12 analyte inside the film, which can lead to faster response time compared to classical MIPs.
13 A comparative study between a MIS and a MIP specific to the iprodione fungicide has
14 revealed better performance for the MIS, including faster permeation and more specific
15 recognition (with imprinting factor of MIS 2.5 times higher than that of the acrylate-based
16 MIP), but also a lower binding capacity of MIS relative to the MIP material.^[108] Note that
17 the open structure of the ORMOSIL is a positive point for getting quite fast response time
18 but it can also result in non-specific binding, requiring to find the best compromise between
19 a sufficient porosity of the film (to ensure fast diffusion processes) and imprinted cavities
20 selective enough for the target analyte.

21 Several examples of electrochemical detection with MIS-coated electrodes are
22 reported in Table 2, which can be distinguished on whether they are made of ORMOSIL
23 alone or containing additives such as nanomaterials or organics.

1 One of the first electrochemical sensors developed on the basis of MIS film was
2 applied to the detection of dopamine (DA) by cyclic voltammetry.^[97] In contrast to non-
3 imprinted films, the DA-imprinted MIS have a satisfactory affinity for dopamine compared
4 to structurally similar molecules such as serotonin, epinephrine, or dihydroxynaphthalene.
5 In another work, MIS films imprinted with tyramine and dopamine also demonstrated good
6 selectivity, with interference levels not exceeding 5%.^[98] A methyl parathion-templated
7 MIS thin film electrodeposited onto a glassy carbon electrode was successfully used for the
8 detection of methyl parathion in pears, exhibiting fast and sensitive response; thanks to
9 effective “ π - π ” interactions and hydrogen bonding in the imprinted cavities, very good
10 selectivity was achieved in the presence of interfering substances such as α -hydroxyl-4-
11 nitrophenyl-dimethyl-phosphonate, *p*-nitrophenol and nitrobenzene, except for parathion
12 (giving a signal of about 50% relative to that of methyl parathion).^[109] Chlorogenic acid
13 determination in hot drinks was achieved using a gold electrode pre-treated with
14 mercaptopropyltriethoxysilane (MPTMS) and covered with a MIS film made of TEOS,
15 phenyltriethoxysilane (PTEOS) and 3-aminopropyltrimethoxysilane (APTMS).^[102]
16 MPTMS served as molecular glue between Au surface and MIS while phenyl and amino
17 groups helped with the probe recognition via electrostatic, hydrogen bonding and “ π - π ”
18 interactions (Fig. 3B). Polyelectrolytes can be also added to the MIS in order to induce
19 positive or negative charges that are likely to affect the probe binding process, as reported
20 for the voltammetric sensing of purine bases (adenine and guanine) in hydrolysed solutions
21 of DNA.^[99] Finally, it is also possible to perform chiral electrochemical recognition using
22 very thin MIS films on ITO electrode, as pointed out for the distinction of enantiomer pairs
23 (respectively (R)- and (S)-N,N'- dimethylferrocenylethylamine and D- and L-3,4-
24 dihydroxyphenylalanine).^[110] In this work, the modified electrode was not directly applied
25 to quantitative determinations but, taking into account the attractiveness of electrochemical

1 chiral analysis,^[111] the elaboration of chiral MIS for electrochemical sensing could be a
2 versatile and rather simple way to achieve this goal by avoiding the need to elaborate very
3 sophisticated multicomponent systems.^[112]

4 On the other hand, nanomaterials possessing electrocatalytic activity towards the
5 target analytes can be successfully associated to MIS, forming sensitive nanocomposite
6 layers on the electrode surface. Examples are available for graphene oxide (GO),^[100] multi-
7 walled carbon nanotubes (MWCNT),^[74, 101, 103, 104, 106, 107, 113] and noble metal
8 nanoparticles.^[105, 114] As for other types of silica-based composite film sensors (section
9 3.1.2), the introduction of such nanomaterials into the MIS contributes to enhancing the
10 electron transfer rates, the electroactive surface area of the electrode and thus the sensitivity
11 of the electrochemical sensing, the selectivity of the detection originating again from the
12 imprinted cavities in the film. Several sensors with good analytical performance have been
13 reported. Paracetamol was determined in tablets and human urine using a phenyl-
14 functionalized MIS comprising GO deposited on glassy carbon electrode (GCE).^[100] A very
15 stable and sensitive electrochemical sensor for benzylpenicillin in blood plasma was
16 constructed on carbon electrode modified with multiwalled carbon nanotubes (MWNTs)
17 decorated with Fe₃O₄, doped with chitosan and covered with MIS film; the sensor exhibited
18 good selectivity for benzylpenicillin in the presence of streptomycin, clindamycin, oxacillin
19 and erythromycin, or 100-fold excess of ascorbic acid, dopamine and uric acid.^[104] A layer-
20 by-layer construction method was applied to develop a sensitive and selective
21 electrochemical sensor for the determination of L-phenylalanine in blood plasma and other
22 physiological fluids.^[106] It is based on aniline electropolymerization on a carbon electrode
23 to get a polyaniline (PANI) layer, its subsequent coverage with β -cyclodextrin (β -CD)
24 incorporated MWNT, and final covering with MIS film obtained by EAD (Fig. 3C)
25 Selectivity factors towards the stereoisomer D-phenylalanine was 0.23, and it was even

1 much better (ranging between 0.09 and 0.12) for L-proline, DL-methionine, L-histidine, and
2 L-norleucine, confirming a good selectivity for L-phenylalanine.^[106] A composite film made
3 of TEOS–CTAB-based MIS combined with L-histidine-functionalized MWCNT and
4 poly(dimethylsiloxane) on GCE was applied to the ultrasensitive (pM range) detection of
5 tetracycline in pharmaceutical capsules, human serum and tap water, with good selectivity
6 over anthracyclines.^[113] Other examples involving MWCNTs and MIS nanocomposite films
7 have been described the determination of thymidine in tablets,^[107] naloxone in urine,^[74.] or
8 L-histidine in human blood serum,^[101] always with good selectivity over structurally-related
9 compounds. GCE modified with MWCNTs/vinyl-functionalized MIS film was reported to
10 be a good sensor for caffeine in coffee and energy drinks, with quite fast response time
11 (maximum response after 15 min incubation time), yet with few non-specific binding of
12 some analogues (xanthine, theophylline, theobromine) but they did not interfere with
13 caffeine determination as they appeared at different potential values.^[103] Finally, gold
14 nanoparticles (AuNPs) can also contribute to improving the response of MIS-based
15 electrochemical sensors. For example, a composite film made of chitosan and phenyl-
16 functionalized MIS encapsulating *p*-nitrophenol and AuNPs was electrogenerated in one
17 step on GCE and the resulting electrode applied for the selective detection of *p*-nitrophenol,
18 with 6-fold enhancement of the voltammetric signal compared to *m*-nitrophenol, *o*-
19 nitrophenol and 2,3-difluoro-*o*-nitrophenol (Fig. 3D).^[114] A sensor for bisphenol A
20 combining both MWCNTs and AuNPs with an amino-functionalized MIS thin film
21 obtained by EAD was also described, exhibiting a particularly good selectivity (only 15%
22 of the signal corresponding to 3 μ M bisphenol A was observed in solutions containing
23 phenol, 1,4-dihydroxybenzene or 4-*tert*-butylphenol at the much higher concentration of 3
24 mM).^[105]

25 **3.2. Composite films based on ordered mesoporous silica**

1 With rare exceptions,^[115-120] most electrochemical sensors involving ordered
2 mesoporous silica films on electrodes are based on the use of vertically aligned nanochannel
3 membranes prepared either by EASA^[121-157] or Stöber growth,^[158-180] or even both these
4 methods^[181, 182] (Table 3). They will be noted as vertically-oriented mesoporous silica film
5 (VMSF) hereafter. Several kinds of composite films can be distinguished: (1) those made
6 of the mesoporous silica film filled with the organic template used for its synthesis (mainly
7 surfactants^[25-27, 33, 137] but also coordination polymers^[183]), mainly deposited on flat
8 electrode surfaces as indium-tin oxide (ITO)^[163, 164, 173, 175, 177, 178] or electrodeposited as
9 nanocomposite films around reduced graphene oxide;^[125] (2) those made of surfactant-
10 extracted mesoporous silica electrodeposited as nanocomposite films around various kinds
11 of nanocarbons (reduced graphene oxide, three-dimensional graphene, carbon nanotubes or
12 graphene-carbon nanotube assemblies);^[121, 123-125, 128, 130, 138, 140, 146, 149, 153, 155, 156] (3) a wide
13 range of chemically modified mesoporous silica films that can be basically divided further
14 in two categories depending on whether they contain organo-functional groups (either
15 weakly immobilized^[126, 129, 139, 145, 162, 165, 166, 169, 171, 172, 176, 179, 180] or strongly attached via
16 covalent bonds^[116, 118-120, 122, 126, 127, 131, 133, 134, 136, 137, 143, 147, 150-152, 157, 160, 161, 174]) or serve as
17 hosts for nano-objects (such as polymers^[140, 141, 158] or nanoparticles^[159, 167, 168, 170, 181, 182]);
18 and (4) other composites made of ordered silica films combined with other nanomaterials
19 (such as clays,^[117, 132, 135] for instance). An illustrative summary of the various sensing
20 applications of composite electrodes made of VMSF materials, respectively with filled
21 pores, open pores and functionalized pores, is given in Figure 4. The main analytical/sensing
22 schemes are based on permselectivity, preconcentration electroanalysis, direct or indirect
23 detection, electrocatalysis and apta- or immunosensing. VMSF films with filled pores can
24 be used for hydrophobicity-based preconcentration and anti-fouling selective detection, or
25 even for mediated electrocatalytic detection when the template is electroactive. VMSF films

1 with open pores of nanometric dimensions are characterized by size and charge selectivity
2 at the molecular scale,^[26, 27] which can be exploited in permselective sensing involving
3 preconcentration/rejection associated to electrochemical detection or for enhanced
4 electrochemiluminescence sensing due to the accumulation of the cationic probes. Finally,
5 the various ways to modify VMSF films lead to a series of reactive surfaces (with anchoring
6 ligands, metal nanoparticles, conductive polymers, redox-active moieties, or diagnostic
7 reagents such as aptamers-antibodies, for instance), which are likely to be exploited in
8 several electrochemical sensing applications. They encompass selective preconcentration
9 and detection, direct and mediated electrocatalysis, indirect amperometric detection or
10 signal transduction of hybridization events. They are briefly described and discussed
11 hereafter by type of composite materials, based on the data provided for various analytes
12 and electrode configurations in Table 3.

13 *3.2.1. Ordered silica films with surfactant in the nanochannels*

14 Such composite films on ITO electrodes have been exploited for the extraction and
15 subsequent electrochemical determination of lipophilic analytes (drugs, pesticides,
16 explosives) in real media without pre-treatment thanks to their anti-(bio)fouling properties.
17 The small molecules are accumulated in the surfactant phase and electrochemically detected
18 whereas ionic species and large molecules (*i.e.*, larger than the nanochannels diameter) are
19 excluded from reaching the underlying ITO surface. Examples are available for the analysis
20 of chloramphenicol in human whole blood^[163] or in milk and honey samples,^[164]
21 antioxidants (retinol, Trolox) in fruit juices,^[177] nitroaromatic explosives and pesticides in
22 water samples or foodstuffs,^[175] halonitrobenzene derivatives in lake water and soil
23 dispersion,^[173] or the tetramethylbenzidine (TMB) substrate.^[178] The depletion of TMB
24 catalyzed by G4zymes can be also used to detect biomarkers (ATP, thrombin, DNA) in

1 complex biological samples.^[178] The calibration curves were most often characterized by
2 two linear ranges, being more sensitive at low concentration due to more effective
3 preconcentration.^[163, 173, 175] The effectiveness of the analyte accumulation into the film is
4 demonstrated by much larger sensitivity than on bare ITO electrodes.^[163, 164] All neutral
5 species are in principle likely to be dissolved in the surfactant phase but only the lipophilic
6 ones are efficiently extracted and thus preconcentrated, as pointed out for a mixture of
7 dihydroxybenzene isomers (*e.g.*, the more hydrophobic catechol is much more effectively
8 accumulated via hydrophobic interactions than the rather hydrophilic hydroquinone).^[125]
9 Note that, in turn, hydroquinone can be accumulated via hydrogen bonding to the silica
10 surface (*i.e.*, after removal of the surfactant), but this falls under the next section 3.2.2.

11 A special case is that of mesoporous silica film prepared from an electroactive
12 structure-directing agent (such as the coordination polymer made of iron triazole complexes
13 $\text{Fe}(\text{Htrz})_3$ ^[183]), which can be used itself as a redox mediator for the electrocatalytic detection
14 of the analyte, as demonstrated for hydrogen peroxide sensing.^[141]

15 3.2.2. Surfactant-free ordered silica films electrodeposited onto nanocarbons

16 After the surfactant has been removed, the resulting widely open mesoporous films
17 with vertically aligned nanochannels enable very fast mass transport from the solution to
18 the electrode surface,^[24, 54, 60] being attractive to impart high sensitivity to the
19 electrochemical detection of target analytes.^[16, 27, 184] Selectivity can be also induced by the
20 film as only analytes smaller than the mesopore aperture are likely to cross the film, the
21 larger ones being excluded (*i.e.*, size selectivity),^[70] while cationic species are preferably
22 accumulated (and anions repelled) due to electrostatic attractions (repulsions) by the
23 negatively charged silanolate groups present on the silica surface (*i.e.*, charge selectivity).^[69]
24 Note that charge selectivity can be tuned by adjusting pH and/or ionic strength of the

1 medium, by modifying the surface charge of the material (turning silanolate into protonated
2 silanol groups, for instance) or by changing the thickness of the electrical double layer in
3 the nanochannels.^[26, 27, 185] An important point for application is the good adhesion of the
4 film to the electrode surface, in a mechanically stable form after the surfactant removal.
5 This is intrinsically the case of silica films on ITO electrodes (thanks to their surface
6 hydroxyl groups),^[61] but it may require the use of a “molecular glue” for other supports,
7 such as electrografted aminopropyltriethoxysilane on carbon electrode^[186] or chemisorbed
8 mercaptopropyltrimethoxysilane on a gold electrode.^[187] Another strategy is the
9 electrochemical activation of carbon supports to generate surface-active groups likely to
10 ensure the durable attachment of EASA-produced mesoporous silica films.^[188] This has
11 been largely applied to the electro-assisted deposition of VMSF around nanocarbon
12 supports and the use of the resulting nanocomposite films for electrochemical sensing.^{[121,}
13 123-125, 128, 130, 138, 142, 147, 149, 153, 155, 156]

14 Many examples are given in Table 3 for the determination of various analytes,
15 including drugs or pharmaceuticals,^[128, 130, 138, 146] neurotransmitters^[121, 164] or other
16 biologically relevant molecules,^[121, 153, 156, 164] pesticides,^[124, 142, 144, 148, 149, 155] and
17 hydroquinone derivatives.^[123, 125] In many cases, the analytical procedure clearly involves
18 the accumulation of the analyte in the film prior to its electrochemical detection on the
19 electrode substrate (*i.e.*, by electrostatic binding of cations^[121, 128, 130, 142, 146, 148, 149, 153, 164] or
20 the formation of hydrogen bonds^[123, 125, 153, 155] or both,^[156] or via electro-
21 oligomerization^[144]), but in some cases it is difficult to make a real distinction between a
22 possible preconcentration in the film and a direct electrocatalytic detection on the
23 nanocarbon surface, both being expected to enhance the voltammetric signals. Also,
24 synergetic effects and electrocatalytic behaviour are sometimes claimed^[124, 142, 149] but rarely
25 demonstrated by both a signal enhancement and a noticeable decrease in the

1 overpotentials.^[121, 146, 155] As above (section 3.2.1), the calibration curves may show two
2 distinct linear ranges, with higher sensitivity at lower concentration due to more effective
3 preconcentration ability (as demonstrated, for example, for paraquat detection^[148, 149]
4 showing unambiguous adsorption behaviour at low concentration and an adsorption-
5 diffusion regime in more concentrated solutions,^[148] enabling efficient trace analysis in the
6 nM range). Again, the anti-fouling and anti-interference features of the VMSF can be
7 exploited for the analysis of real media, as exemplified for biologically relevant molecules
8 in human serum,^[121, 156] or drugs in whole blood or urine samples.^[130, 138, 146] In these cases,
9 the mesoporous silica film acts as a real molecular filter enabling the small analytes to reach
10 the electrode surface and being detected without (bio)fouling because bigger molecules
11 cannot cross such physical barrier (as explicitly pointed out for propranolol detection in the
12 presence of haemoglobin,^[189] for instance). Of related interest is the label-free
13 electrochemical detection of protein kinase activity and inhibition in the presence of a redox
14 probe in solution, by distinguishing between the large currents observed in case of peptide
15 cleavage and the hampered diffusion of the redox probe through the film in the absence of
16 cleavage (due to the adsorption of the phosphorylated peptide).^[190] Finally, one has to
17 mention that only few stability data are available (Table 3), which might be an issue for
18 VMSF made of silica gel-based walls. Actually, the operational stability in aqueous
19 solutions is limited to few measurements (typically five^[146, 155]) and rather short times (10-
20 30 min^[123, 138, 153]), suggesting to consider their utilization primarily as components of
21 single-use sensors.

22 3.2.3. Ordered silica films doped with analytical reagents

23 The accumulation ability of VMSF, notably towards cationic species, can be
24 exploited to dope such films with suitable analytical reagents that are usually used in

1 solution, with the idea to concentrate them close to the electrode surface. This has been
2 basically developed for enhancing the electrochemiluminescence (ECL) of $\text{Ru}(\text{bpy})_3^{2+}$ on
3 ITO electrodes modified with VMSF. The concept was first reported from a model system
4 involving the use of tri-*n*-propylamine (TPrA) as the coreactant and a dilute solution of
5 $\text{Ru}(\text{bpy})_3^{2+}$ (9 μM).^[180] Thanks to strong electrostatic attraction, $\text{Ru}(\text{bpy})_3^{2+}$ cations are
6 accumulated onto the silica walls and both these species and TPrA molecules are diffusing
7 very fast in the oriented nanochannels, contributing to ECL signals larger by *ca.* two orders
8 of magnitude for the film electrode as compared to bare ITO, as demonstrated for the
9 detection of not only TPrA but also atropine and nicotine^[180] (notably in commercial
10 products for nicotine^[172]). It was then extended to the analysis of aromatic explosives^[179] or
11 dopamine^[165] with a smartphone-based ECL system involving VMSF on disposable screen-
12 printed carbon electrodes or ITO electrodes. Further researches were devoted to build ECL
13 devices based on VMSF generated onto other supports such as paper μchips ^[171] or
14 polyethyleneterephthalate coated with indium-tin oxide^[129] as flexible composite electrodes
15 for the electrochemical sensing of drugs or antibiotics in biological samples. To avoid
16 possible reagent leaching in the external solution, a second VMSF layer bearing positively
17 charged groups can be overcoated onto the $\text{Ru}(\text{bpy})_3^{2+}$ -loaded one, the effectiveness of the
18 approach being demonstrated by multiple successive cyclic voltammetry (CV) or ECL
19 experiments (no noticeable signal change after 24 cycles, compared to the intensity drops
20 by 31% and 48% respectively observed for CV and ECL measurements).^[127] Most systems
21 were based on VMSF generated by the Stöber growth method, except one example
22 (lidocaine sensing in serum^[145]) confirming that the EASA-based films can be also useful
23 for manufacturing ECL devices. The other silica-based ECL sensors are presented in section
24 5.1. Finally, one has to mention that $\text{Ru}(\text{bpy})_3^{2+}$ -loaded VMSF on ITO electrode have been

1 applied as electrocatalytic sensors for the mediated detection of guanine in beer and
2 pharmaceuticals.^[139]

3 *3.2.4. Ordered silica films bearing covalently attached organo-functional groups*

4 A good way to circumvent the problems associated to the loosely bound reagents
5 in VMSF is the use of covalently functionalized films.

6 A first category includes VMSF with organic groups grafted only on top of the
7 silica membrane (*i.e.*, not inside the nanochannels). They are prepared either by coating or
8 by grafting the film prior to surfactant extraction. For example, VMSF covered with
9 polydimethylsiloxane on top facilitates greatly the transport of small hydrophobic molecules
10 through the film while acting as a barrier for the hydrophilic ones (flux differences by *ca.*
11 3-4 orders of magnitude),^[174] enabling the electrochemical sensing of non-polar molecules
12 such as bisphenol A in wine^[160] or paraoxon in milk.^[174] A second example encompasses
13 the geno-, immuno- or aptasensors made of VMSF functionalized respectively with a
14 gene/DNA strand, an antibody, or an aptamer, covalently grafted on top of the oriented
15 mesoporous silica membrane, and operating with a redox probe in solution.^{[126, 131, 136, 143,}
16 ^{150-152, 161]} Upon hybridization with the complementary strand (DNA/antigen/aptamer)
17 acting as the analyte, there is less space available for the redox probe to cross the so-
18 functionalized membrane and to reach the electrode surface (see illustration in extreme right
19 of Fig. 4), leading to a lower electrochemical signal. This current decrease is proportional
20 to the analyte (DNA, antigen, or aptamer) concentration in solution, constituting therefore
21 the signal transduction of the recognition event. This electroanalytical scheme has been
22 applied to the genosensing of DNA,^[136] the immunosensing of tumor antigen CA15-3,^[126]
23 C-reactive protein,^[131] or prostate specific antigen (PSA),^[150, A151] and the aptasensing of
24 cardiac troponin I,^[161] insulin,^[143] or PSA,^[152] their corresponding analytical performance

1 being given in Table 3. Otherwise, DNAzyme attached on top of VMSF can be activated by
2 copper and ascorbic acid species and its molecular switching is likely to control the diffusion
3 of a redox probe from the solution to the underlying electrode surface, this system acting
4 thus as a molecular gate for the indirect detection of those analytes.^[122] Of related interest
5 is the grafting of i-motif DNA moieties whose changes in confirmation around physiological
6 pH is likely to regulate the diffusion of a redox probe through the film, resulting in a pH-
7 dependent amperometric response that has been applied for pH monitoring in brain
8 microdialysates.^[176]

9 A second category is made of organic ligands or other preconcentration agents
10 covalently attached onto the internal surface of the nanochannels. The interest of the ordered
11 mesoporous silica supports in this case is the possibility of having hybrid materials carrying
12 a high density of organo-functional groups easily and quickly accessible for the species in
13 solution,^[191, 192] much better than the non-ordered analogous silica-based adsorbents,^[193]
14 which helps provide sensitive electrochemical detection when used as electrode
15 modifiers.^[16, 25] Glassy carbon or gold electrodes coated with VMSF bearing organic ligands
16 such as amine,^[133] thiol^[116, 119] or 5-mercapto-1-methyl-tetrazole,^[118] can be applied to the
17 preconcentration of metal ions (Ag^+ , Cu^{2+} , Hg^{2+}) and their detection by anodic stripping
18 voltammetry. When protonated, the amine groups become cationic and are likely to
19 accumulate analytes that are negatively charged at physiological pH, such as tryptophan or
20 uric acid, which are then electrochemically detected on the underlying electrode surface.^{[120,}
21 ^{157]} Effective preconcentration by electrostatic attraction is also achieved with VMSF
22 functionalized by quaternary ammonium groups, as pointed out for the selective detection
23 of ascorbic acid in the presence of dopamine, the opposite selectivity being obtained on non-
24 modified VMSF electrode.^[137]

1 A third category is that of VMSF functionalized with electroactive moieties.
2 Combining EASA with click chemistry has proven to be an effective method to get oriented
3 mesoporous silica films with redox-active groups covalently attached to the mesopore walls,
4 such as metallocenes,^[63-65] iron polypyridine complexes^[194, 195] or tetrazine derivatives,^[196]
5 while keeping their electrochemical activity and/or their photophysical properties. In such
6 an electrically insulating film, the overall charge transfer mechanism involves an electron
7 hopping between adjacent redox species (electron transfer), most often combined to mass
8 transport implying the electrolyte ions (to maintain charge balance). The interplay between
9 both processes is influenced by the density of redox-active groups in the material as well as
10 the nature and concentration of electrolyte ions in solution.^[65] From the electrochemical
11 sensing point of view, only ferrocene functionalized VMSF has been exploited so far. The
12 first conceptual application is the indirect amperometric detection of non-electroactive
13 anions that act as charge compensating species during the oxidation of ferrocene into
14 ferricinium, the measured currents being proportional to the concentration of these anions
15 and the signal is made of both faradic and capacitive contributions as one needs to operate
16 in electrolyte-free medium.^[147] The detection of several anions in mixture is also possible
17 by using the sensor at the output of an ion chromatograph. A second application is based on
18 the mediator properties of the ferrocene groups, which can be exploited for the
19 electrocatalytic detection of cysteine and glutathione with a marked selectivity for the
20 former thiolated compounds most probably because of the confined space of mesopore
21 channels.^[134] Electrocatalysis with mediators immobilized in non-ordered silica films has
22 been otherwise reported for biosensing applications (see section 4), but to date not yet with
23 VMSF probably due to the difficulty to accommodate redox proteins or enzymes in
24 mesopores of so small diameters.^[197]

25 3.2.5. *Ordered silica films as hosts for nano-objects*

1 VMSF can be used as host for metallic nano-objects generated electrochemically
2 by reduction of metal precursors (*i.e.*, PtCl_6^{2-} or AuCl_4^-) at the bottom of the nanochannels.
3 Sometimes, the VMSF material was functionalized beforehand with ammonium moieties to
4 induce a positive charge likely to accumulate the precursor anions.^[159, 170] Supported Pt
5 nanostructures/nanoparticles^[182] and Au nanoparticles^[170] have been obtained and exploited
6 for their conductive and/or electrocatalytic properties, for the electrochemical sensing of
7 hydrogen peroxide^[170, 182] or ascorbic acid,^[159] for instance. NiO(OH) nanostructures were
8 also electrodeposited in VMSF and applied to the non-enzymatic detection of glucose,^[167]
9 but surprisingly in 0.1 M NaOH, a medium in which the silica film is not expected to survive
10 (dissolution occurs in strong alkaline medium^[198]). A last example is the nano-confinement
11 by electrophoresis of small graphene quantum dots in VMSF and their use for signal
12 amplification in the electrochemical sensing of heavy metal ions in contaminated seafood
13 samples or soil leaching solutions, and dopamine in serum samples.^[181]

14 Otherwise, conducting polymer nanofilaments such as polyaniline (PANI) can be
15 electropolymerized in a controlled way through the nanochannels of VMSF using the silica
16 membrane as a hard template.^[199] The obtained mesoporous silica/PANI composite exhibits
17 electrocatalytic properties usable for the anodic detection of ascorbic acid and can be also
18 exploited for pH sensing.^[158] When additional Pt nanoparticles are generated in the
19 composite, thanks to the favorable interactions between PtCl_6^{2-} and PANI, the resulting
20 electrode is a good electrochemical sensor for hydrogen peroxide over a wide concentration
21 range (μM – mM).^[169] Of related interest are Prussian Blue nanowires electrochemically
22 grown through VMSF and also applied to the electrocatalytic detection of hydrogen
23 peroxide.^[140]

24 3.2.6. Composites made of ordered silica films and other nanomaterials

1 This last category relates to more heterogeneous deposits prepared either by taking
2 advantage of the possibility to combine the EASA method with the entrapment of clay or
3 organoclay particles in VMSF on electrode,^[132, 135] or by generating silica-based
4 nanochannels in the interlayer spacings of swelling clays to form so-called porous clay
5 heterostructures as thin films on an electrode surface.^[117] The interest of such composites is
6 to combine the recognition/accumulation properties of the (organo)clays with the fast mass
7 transport ensured by the ordered mesoporous silica matrix. They have been applied to the
8 preconcentration electroanalysis of metal ions (Hg^{2+} ,^[117] Cu^{2+} ^[132]) or nonsteroidal anti-
9 inflammatory drug (diclofenac^[135]).

10

11 **4. Electrochemical biosensors**

12 Silica films obtained by the sol-gel method are widely used for the encapsulation of
13 biomolecules and their immobilization onto electrode surfaces; they hold a good position
14 among electrodes modified with other nanomaterials.^[200-204] The encapsulation of
15 biomolecules (*i.e.*, enzymes) inside silica thin films helps to place them as close as possible
16 to the conductive surface of the electrode. The polymeric framework prevents the
17 biomolecules from leaching and contributes to protect them from the influence of aggressive
18 surrounding environments. At the same time, the quaternary structure and conformational
19 mobility of proteins entrapped inside silica film remain intact. Contrary to biosensors based
20 on organic polymers, those based on biologically modified silica materials possess a porous
21 three-dimensional rigid structure which makes proteins encapsulated inside the film
22 accessible to the substrate. Bioelectrochemical sensors based on composite silica films are
23 characterized by high catalytic activity and long-term stability. Both three-dimensional and
24 planar electrodes are used as supports for bio-silica films as the sensitive elements of

1 biosensors. Among them, devices involving the use of planar printed electrodes are
2 becoming widespread in recent times as disposable sensors for measurements outside the
3 laboratory.^[205, 206] They are significantly cheaper than three-dimensional sensors and
4 usually easier to modify. They are compatible with the analysis of small sample volumes
5 (5-10 μ l) in biochemical and medical monitoring, suitable for quality control of food
6 products, and attractive for on-site characterization of environmental media, etc. Planar
7 electrodes can be connected to a smartphone, which plays the role of transducer.^[206] The
8 modification of planar screen-printed electrodes (Fig 5A) with silica-based biocomposite
9 thin films is thus a perspective way for the development of disposable sol-gel biosensors.

10 There are a lot of reviews dealing with electrochemical sensors based on
11 biomolecules encapsulated in silica materials,^[7-10, 13, 200, 201, 207-209] some of them
12 considering also the uniform silica-based biocomposite films.^[13, 200, 201] Most often,
13 protein molecules are mixed with the silica sol before being applied to the surface of the
14 electrodes, the biomolecule being physically entrapped during gelation. Among the methods
15 of depositing biocomposite films onto electrode surfaces (Table 4), one can highlight those
16 based on evaporation (*i.e.*, spin-coating (rotation), dip-coating (immersion), drop casting or
17 spraying), layer-by-layer (LbL) growth, and electrochemically-assisted deposition (EAD).
18 The two first give the possibility to work mainly with smooth and flat electrode surfaces
19 (evaporation) or involve time consuming procedures (LbL), whereas the third one (EAD)
20 offers the advantage of being easily applied to the modification of electrodes with
21 complicated geometry including macroporous electrodes,^[34, 210] carbon nanotube
22 assemblies,^[37, 211] or screen-printed electrodes^[212, 213] (an illustration of the EAD process on
23 a screen-printed electrode is shown in Fig. 5B). It permits to bring proteins as close as
24 possible to the conductive electrode surface, which helps to detect electrochemically the
25 active center of the encapsulated enzymes during the biocatalytic cycle.^[37, 214] As mentioned

1 above (section 3.2.4), it also enables the generation of ordered silica films supporting
2 covalently-attached genes, antibodies or aptamers.^[126, 131, 136, 143, 150-152, 161] By offering an
3 easy way to immobilize biomolecules by weak (encapsulation) or strong (covalent) bonding,
4 the sol-gel process opens up wide possibilities to create the sensitive elements of third-
5 generation mediatorless biosensors.

6 Several examples of electrochemical biosensors integrating electrodes modified
7 with silica-based biocomposite thin films are given in Table 4; they are discussed below by
8 distinguishing the various families of materials.

9 **4.1. Bioelectrodes based on sol-gel bioencapsulation**

10 A straightforward way to confine proteins in silica films deposited onto electrode
11 surfaces is their direct entrapment during the silica polycondensation by the so-called sol-
12 gel bioencapsulation for biosensors.^[22] As pioneers, Nadzhafova *et al.*^[40] and Jia *et al.*^[41]
13 reported the one-step immobilization of glucose oxidase and/or haemoglobin by
14 electrochemically induced sol-gel bioencapsulation. The encapsulated biomolecules (Fig
15 5C) were electrochemically accessible (*i.e.*, redox-active^[34]) and they kept their biological
16 activity (*e.g.*, possibility to detect glucose^[40, 41]). Similar bioceramic thin films can be
17 prepared by spin-coating or dip-coating on electrodes and exploited as electrochemical
18 biosensors.^[215] Both sol-gel bioencapsulation methods are compatible with the co-
19 entrapment of nanoparticles (Fig 5D) to improve the bioceramic properties (notably its
20 electrical conductivity). Atomic force microscopy can be used to evidence the formed
21 bioceramic films (Fig 5E). However, such simple approaches might result in non-efficient
22 bioencapsulation and poor electrochemical or biocatalytic responses,^[210] requiring the use
23 of suitable additives (polymers, surfactants, nanoparticles) or functionalization strategies

1 (with charge transfer cofactors) to get biosensors with enhanced performance, as described
2 hereafter.

3 **4.2. Silica-polymer biocomposite films**

4 A way to improving the analytical characteristics of the electrodes modified with
5 biocomposite films is to introduce conductive polymers, polyelectrolytes or polysaccharides
6 into the starting silica sol, which are intended to form interpenetrated organic-inorganic
7 networks (see right part (b) in Fig. 1B). It helps to fix the proteins more firmly inside the
8 composite film due to electrostatic and hydrophobic interactions and it may also enhance
9 the electrical conductivity (in case of conducting polymers) and plasticity of the bioceramic
10 films. Various kinds of (macro)molecules are used for such purpose. Among them one can
11 mention: polyaniline,^[216] poly(ethyleneimine),^[217] poly(vinyl alcohol),^[77] poly(styrene
12 sulfonic acid) or polydimethyldiallylammonium chloride,^[37] or even ionic liquids.^[218, 219]
13 The biosensors based on such films are usually characterized by better stability and
14 sensitivity due to increased amount of protein molecules firmly fixed in an active form and
15 accessible for the substrate. For example, the natural polysaccharide Chitosan has good
16 affinity to protein molecules, thus improving the plasticity of the films when used as additive
17 to silica biocomposites.^[51] Enzyme immobilization within sol–gel silica and poly(vinyl
18 alcohol) on screen-printed electrodes according to a one-step process was even reported to
19 achieve direct electrochemistry of glucose oxidase,^[77] the observed electrochemical
20 response being however most probably due to the prosthetic flavin adenine dinucleotide
21 moieties, which may have dissociated away from the immobilized enzyme or else coming
22 from impurities.^[220] Direct electron transfer was further demonstrated for a smaller redox
23 protein, hemoglobin (Hb), immobilized in a PANI–SiO₂ film also containing a surfactant
24 (dodecyltrimethylammonium bromide, DTAB).^[216] When deposited onto the surface of a

1 carbon paste electrode (CPE), the resulting Hb/PANI–SiO₂/DTAB/CPE biocomposite
2 electrode demonstrated fast electron transfer processes for Hb, with an electron transfer rate
3 constant of about 0.94 s⁻¹. This system was used as a highly sensitive biosensor for hydrogen
4 peroxide thanks to the excellent electrocatalytic activity of Hb for the reduction of H₂O₂.
5 The conductivity of PANI and the protective action of DTAB can provide a favourable
6 microenvironment for redox proteins and enzymes, opening the door to other potential
7 applications in direct electrochemistry biosensors and bioelectrocatalysis. In a different
8 domain, a biocomposite film made of silica gel, an ionic liquid (1-amyl-2,3-
9 dimethylimidazolium hexafluorophosphate) and a non-ionic surfactant (Triton X-100) on
10 glassy carbon electrode was used for the immunosensing of aflatoxin B1 (AFB1).^[218] The
11 ionic liquid offered a biocompatible microenvironment for AFB1 antibody while Triton X-
12 100 ensured the formation of a crack-free film. The resulting label-free immunosensor
13 operated based on electrochemical impedance measurements and presented better
14 sensitivity (2-fold) and much longer stability (190- fold) than the corresponding undoped
15 silica gel immunosensor.

16 **4.3. Biocomposite films based on silica-surfactant or functionalized silica materials**

17 The surfactants are widely used in the formation of biocomposite films as they can
18 behave either as structure directing agents (leading to porous and often ordered materials
19 with enhanced accessibility, as those described in section 3.2), or as stabilizers for the
20 biomolecules in the composite layer, or as both of them. For example, the cationic surfactant
21 CTAB at its critical micellar concentration level helps distribute the proteins more
22 uniformly in the biocomposite film via a better solubilisation in the silica sol. This leads to
23 increasing amounts of the electroactive proteins (*e.g.*, Hb) encapsulated inside the
24 biocomposite film, which remain accessible for the substrate, thus resulting in enhanced

1 sensitivity and long-term operational stability the developed biosensors.^[212] This is also
2 demonstrated for enzymes, such as choline oxidase entrapped in a biocomposite film on
3 gold screen-printed electrode by electrochemically assisted sol-gel deposition, giving rise
4 to a mediator-free choline biosensor with enhanced stability (over 3 weeks) when using the
5 cationic surfactant CTAB in the electrodeposition medium.^[221] Of related interest is the
6 immobilization of other biological materials such as aptamers or antibodies onto the surface
7 of ordered mesoporous silica films prepared with surfactant templates and the exploitation
8 of their modulated permeability to redox probes upon hybridization as transduction mode
9 in electrochemical aptasensors and immunosensors. Actually, silica-based electrochemical
10 immunosensors recently gained much importance for detecting antigens and biomarkers
11 responsible for cancer diagnosis and the determination of some biological molecules.^[208]
12 This has been mentioned above (see section 3.2.4) for aptamers and antibodies covalently
13 grafted to the surface of vertically oriented silica nanochannels,^[126, 131, 136, 143, 150-152, 161] but
14 a softer attachment approach can be also used. This has been notably demonstrated for the
15 label-free electrochemiluminescence (ECL) aptasensing of lysozyme, adenosine and
16 potassium cations.^[222] The principle (Fig 6A) implies the use of an amine-functionalized
17 vertically oriented mesoporous silica film on a transparent ITO electrode filled with
18 luminescence reagents $\text{Ru}(\text{bpy})_3^{2+}$ and covered with the aptamer (Fig 6A₁) interacting with
19 the amino groups via non-covalent electrostatic interactions. In the presence of the target
20 analyte, the mesopores became uncapped due to the specific aptamer-target binding and the
21 release of $\text{Ru}(\text{bpy})_3^{2+}$ species resulted in a decrease in the ECA signal (Fig 6A₂),
22 proportionally to the target analyte concentration. This is a quite versatile approach enabling
23 the determination of enzymes, small molecules, and ions, based on a simple competitive
24 procedure and probably easily transferable to the detection of other analytes by altering the

1 aptamer sequence without any need for its chemical modification (contrary to those grafted
2 covalently).

3 An additional interest of silica-based materials is their ability to be functionalized in
4 a covalent way by exploiting the rich chemistry of organosilane reagents, and this is of
5 particular interest in bioelectrochemistry. An illustration (Fig 6B) is given for reagentless
6 biosensors for D-glucose, D-sorbitol and D-lactic acid elaborated by coating glassy carbon
7 electrodes with biocompatible composite films made of sol-gel silica and ferrocene-
8 functionalized poly(ethyleneimine), encapsulating a bienzymatic system (the appropriate
9 dehydrogenase enzyme and a diaphorase), and attaching the NAD⁺ cofactor to the silica
10 matrix using a suitable organosilane reagent (*i.e.*, glycidopropyltrimethoxysilane, GPS) (Fig
11 6B₁). Such strategy allowed the durable immobilization of the cofactor while its ‘simple’
12 entrapment led to its rapid leaching out of the biocomposite film.^[217] The resulting
13 reagentless device offered good long-term operational stability (more than 12 h of
14 continuous use under potentiostatic conditions in stirred medium whereas very fast
15 deactivation was observed without GPS, see Fig 6B₂ for the particular case of D-sorbitol
16 detection). This constitutes an illustration of the interest of sol-gel-derived biocomposites
17 integrating all components (enzymes, cofactors, redox mediator) in a durably immobilized
18 form to fabricate reagentless biosensors with good stability. A similar methodology has
19 been applied to wrap carbon nanotubes assemblies with biocomposites by electro-assisted
20 deposition for co-immobilizing D-sorbitol dehydrogenase, an osmium-complex modified
21 polymer or poly(methylene green) as mediator, and NAD-GPS as cofactor, which were
22 applied to the amperometric biosensing of D-sorbitol.^[211, 223]

23 4.4. Silica-nanoparticles biocomposite films

1 Second-generation biosensors using electron mediators, as well as third-generation
2 mediatorless biosensors are of particular interest nowadays. To this end, it is promising to
3 introduce on the electrode surface composites made of biosilica films with encapsulated
4 nanomaterials likely to improve the electrical conductivity of the film and/or to act as
5 electrocatalysts.^[201] Examples of nanomaterials used for that purpose are: nanostructured
6 carbon,^[37, 217, 224, 225] metal nanoparticles,^[51, 200, 212, 221, 226, 227] metal oxide particles,^{[203, 213,}
7 ^{214]} or their combination ^[51, 219, 224]. The nanostructured conductive materials can serve as
8 nanoconductors and/or electron mediators between the encapsulated protein and the surface
9 of the electrode, thus increasing the number of electrochemically accessible protein
10 molecules. Overall, they contribute at increasing the sensitivity of the analyte determination,
11 enhancing the signal-to-noise ratio, and improving the long-term stability of such
12 biosensors.

13 The co-immobilization of nanoparticles within/on silica biocomposite films on
14 electrodes can be realised in several ways (Fig 6C): (a) one-step modification when all film
15 components are mixed with the silica precursors and applied to the electrode;^[77, 212, 214, 226]
16 (b) two-step modification involving the formation of a porous silica layer and its subsequent
17 functionalization with the nano-objects;^[136, 143, 152, 218, 222] (c) the layer-by-layer (LbL)
18 deposition in which the electrode surface is first coated with a layer of nanoparticles (NP)
19 or nanostructured materials and then covered with the silica biocomposite film.^{[37, 51, 213, 217,}
20 ^{219, 224]} Hereafter, we will essentially focus on the first (one-step) and the third (LbL)
21 methods mainly used for the construction of enzymatic biosensors while the second one was
22 mainly carried out for the development of the apta- and immunosensors already presented
23 above.

1 Gold nanoparticles (Au-NPs) are widely used among the metal nanoparticles for
2 such purpose because of the good affinity to proteins and high electrocatalytic activity.^{[202,}
3 ^{219, 224, 226]} On the basis of an electrogenerated silica film entrapping hemoglobin (Hb) and
4 glucose oxidase (GOx) on carbon and gold electrodes, with or without Au-NPs, it was
5 demonstrated that the stability of the analytical response of the resulting bioelectrodes was
6 significantly improved when Au-NPs (20 nm in diameter) were present.^[212, 226]
7 Electrochemical biosensing was possible in real media, as pointed out for glucose
8 determination in porcine blood serum using a SiO₂-Hb-GOx-Au-NPs biocomposite film
9 on a gold electrode.^[226] On the other hand, electrodes modified with Hb were used for the
10 determination of antiviral drugs that inhibit the ability of Hb to bind to oxygen.^[212] The
11 bioelectrochemical devices have been prepared by Hb encapsulation in silica sol-gel films,
12 which were generated by EAD method onto pyrolytic graphite electrodes (PGEs). The
13 stability and electrocatalytic activity of Hb entrapped into SiO₂ network was substantially
14 enhanced in the presence of cationic surfactant (CTAB) and Au-NPs. The electrocatalytic
15 current of dissolved oxygen decreased in the presence of the antiviral drug (rimantadine, an
16 amino derivative of adamantane) which opens the way to the determination of this drug.^[212]
17 Another example is the determination of hydrogen peroxide and nitrite using a bioelectrode
18 made of silica-coated gold nanorods (GNRs@SiO₂) and room-temperature ionic liquid
19 (RTIL) 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) entrapping the redox
20 protein myoglobin (Mb).^[219] As illustrated in Fig 6D, GNRs@SiO₂ provides a favourable
21 microenvironment for the direct electrochemistry of Mb and its electrocatalytic response to
22 H₂O₂, while at the same time ensuring good hosting capability to prevent RTIL from leaking
23 from the electrode surface. The biosensor exhibited high selectivity, good reproducibility,
24 and long-term stability.

1 Beside gold, platinum nanoparticles (Pt-NPs) are promising modifiers of biosilica
2 composite films, notably because Pt-NPs exhibit catalytic activity in relation to hydrogen
3 peroxide, a product of many enzymatic reactions. Platinization gold electrodes modified
4 with 3-aminopropyltriethoxysilane-chitosan (APTES-CS) hybrid gel film and *in situ*
5 immobilized glucose oxidase (GOx), with or without Pt-NPs, were used for sensitive
6 glucose sensing.^[51] The presence of Pt-NPs in the biocomposite films made it possible to
7 reduce the oxidation overpotential of the enzymatically generated H₂O₂ by *ca.* 200 mV. It
8 resulted in both better sensitivity to glucose over a wider linear concentration range, and
9 lower detection limit than the bioelectrode prepared without Pt-NPs. Following the same
10 idea, systems that are even more sophisticated can be prepared, such as the biocomposite
11 film made of GOx encapsulated in a bifunctional silane-ionic liquid reagent and chitosan
12 generated in one-step by electro-assisted deposition on gold electrodes previously modified
13 with reduced graphene oxide and Pt-NPs.^[228]

14 Nanostructured metal oxide materials, including transition metal oxide
15 nanoparticles, also possess good catalytic activity to hydrogen peroxide and other products
16 of enzymatic reactions. They are quite easy to obtain and rather compatible with silica
17 matrices and ITO electrodes because of their similar oxide nature.^[203] Such modifiers are
18 thus attractive for the development of biosensors made of silica-based biocomposite films.
19 Several examples have been reported. Screen-printed electrodes (SPE) modified with oxides
20 of transition metals (MnO₂ or CuO) and bienzymatic composite films were applied to the
21 determination of disaccharides (maltose and sucrose).^[213, 214] The indicator reaction was the
22 catalytic current of hydrogen peroxide, a product of bienzymatic reactions, at SPE/metal
23 oxide. The use of metal oxide has improved the selectivity of sensors, avoiding the
24 interference of ascorbic acid, urea, and other reducing substances. SPE modified with MnO₂
25 particles and bienzymatic silica film with encapsulated GOx and invertase, prepared by

1 EAD technique, was applied to sucrose biosensing in food.^[213] The determination of maltose
2 in beverage products was achieved using an SPE modified with CuO/GOx/maltase/SiO₂
3 biocomposite film.^[214] In another work, horseradish peroxidase (HRP) immobilized on
4 glassy carbon electrode (GCE) with the aid of a silica–hydroxyapatite (HAp) hybrid film
5 was applied to as H₂O₂ biosensing.^[229] The silica/HRP–HAp/GCE was characterized by fast
6 electron transfer rates and good electrocatalytic properties for the mediatorless reduction of
7 H₂O₂, thanks to the cooperative effect of HAp nanoparticles with silica to provide a
8 biocompatible microenvironment for HRP.

9 The use of carbon nanomaterials in the modification of electrodes allows increasing
10 considerably the active surface area and electrocatalytic properties of the electrode, thus
11 improving its sensitivity for analytical determinations. Beside that, carbon nanomaterials
12 have a good affinity to biomolecules.^[217, 225] Carbon nanotubes (CNTs) are suitable catalysts
13 for the oxidation of the NADH coenzyme in NAD⁺-dependent enzymatic reactions, an effect
14 that is even greater for CNTs functionalized with a redox mediator such as ferrocene.^[225]
15 Electrophoretically-deposited CNTs were used as a porous support onto which silica layers
16 encapsulating enzymes from the dehydrogenases group and a cationic polyelectrolyte were
17 generated by EAD, and the resulting biocomposite was reported to be attractive for the
18 amperometric biosensing of D-sorbitol.^[37] Carbon nanodots (CND) and graphene oxide
19 (GO) have demonstrated an excellent affinity to biopolymers and high catalytic activity to
20 the products of several enzymatic reactions happening at electrode surfaces.^[200, 201, 230] An
21 illustrative example is the combination of Au-NPs in silica matrix, along with reduced GO
22 (RGO) and β-cyclodextrins (CD), to generate a composite electrode with enhanced
23 electroactive surface area, which was then exploited to immobilize HRP enzymes to get a
24 bioelectrode sensitive to H₂O₂.^[224] The silica support reduces the crumpled and wrinkled
25 sheet structures of RGO-CD, hence a flatter platform was obtained. Au-NPs acted as tiny

1 nanoelectrodes thereby increasing electrical communication as well as interfacial
2 interaction with RGO-CD. The obtained electrode demonstrated its affinity to enzyme
3 conjugate HRP-adamantane carboxylic acid (ADA) via supramolecular association between
4 CDs and HRP-ADA. Overall, these multiple components exhibited synergistic effects that
5 favored H₂O₂ reduction in the presence of hydroquinone, in a more efficient way than the
6 individual electrocatalytic effects known for Au-NPs and RGO-CD, respectively.^[224] This
7 strategy could find the way to combine metal nanostructures and RGO in silica-based
8 biocomposites to develop novel solid supports for biosensor assembly.

10 **5. Electrochemiluminescence detection and other sensors**

11 **5.1. Sensors based on electrochemiluminescence detection**

12 Electrochemiluminescence (ECL) constitutes a combination of an electro-induced
13 reaction and the visualization of luminescence.^[231] It can become a quantitative
14 measurement when applying a potential to an electrode surface that can generate species in
15 an excited state resulting in the emission of light from luminophores, in proportion to the
16 concentration of a target analyte involved in the process. Two categories of ECL
17 mechanisms are generally reported:^[231] annihilation ECL (in which only the luminophore
18 participates in light emission) and coreactant ECL. The most efficient ECL systems are
19 based on Ru(bpy)₃²⁺/TPrA (where TPrA is tri-*n*-propylamine coreactant) and luminol
20 derivatives/H₂O₂. The well-known mechanism involving Ru(bpy)₃²⁺ luminophore and
21 TPrA coreactant (see illustration in Fig. 7A) is based on two electrochemical oxidations and
22 the redox reaction between the coreactant radical intermediate and the oxidized Ru(bpy)₃²⁺
23 species to give the excited form of the luminophore, which subsequently emits light upon
24 returning to the ground state during energetic electron transfer reaction, but several novel

1 systems have been reported for ECL sensing.^[232, 233] The combination of ECL method
2 within silica-modified electrodes is a quite old story, which has been reviewed for solid-
3 state ECL sensors based on tris(2,2'-bipyridyl) ruthenium complexes,^[234] involving mainly
4 the use of Ru(bpy)₃²⁺-doped silica nanoparticles. Here, we will focus only on the more
5 recent developments of composite materials made of continuous sol-gel-derived silica films.
6 Such porous matrices contribute to improving the stability of luminophores and coreactants
7 immobilised in the film and facilitate the mass transport of electroactive species through the
8 film, increasing the probability of contact between the analytes in solution and the active
9 sites of the support, thus enhancing dramatically the sensitivity of the electrochemical
10 sensors (see examples in Tables 1-3).^[129, 145, 162, 165, 169-172, 179, 180, 235-242] ECL can be also used
11 as a readout signal for the biosensors, providing a high sensitive and selective method of
12 detection of substrates in enzymatic electrochemical biosensors as well as immuno- and
13 aptasensors (see examples in Tables 3&4).^[126, 127, 151, 161, 222, 243-247] They are mostly based
14 on the two commonly used luminophores luminol and Ru(bpy)₃²⁺, this latter offering the
15 advantage to be regenerable unlike luminol which is consumed.

16 Solid-state ECL sensors obtained through immobilizing Ru(bpy)₃²⁺ on the electrode
17 surface could significantly reduce the consumption of reagents and improve the sensitivity
18 of the detection. Ru(bpy)₃²⁺ can be accumulated in either ordered or non-ordered silica
19 matrices via favourable electrostatic interactions,^[129, 145, 165, 167, 172, 179, 180, 235, 236] or even
20 through covalent bonding.^[237] When applied to tri-*n*-propylamine detection, the ECL sensor
21 fabricated by the sol-gel method (non-ordered silica film) led to a detection limit of 5 nM
22 (*i.e.*, three orders of magnitude lower than that from pure Nafion-modified electrodes), with
23 good stability (92% of the signal remaining after being 35 days storage in air).^[235] By
24 comparison, even much better performance can be achieved with a vertically-ordered thin
25 film, with a detection limit 30 times lower (0.17 nM).^[180] Similar ECL sensor platforms

1 based on ordered silica films were developed for the determination of various drugs and
2 biologically-relevant molecules (Table 3) acting as coreactants, with detection limits at the
3 nanomolar level.^[129, 145, 165, 171, 172] Attaching the luminophore by covalent bonding to the
4 silica material (using a tetrasilylated ruthenium tris-bipyridyl chloride complex) enabled to
5 enhance significantly the sensor stability (*i.e.*, 90% response obtained after 8 hours of
6 continuous use or 6 month storage), but at the expense of lower sensitivity (1 μ M detection
7 limit) due to restricted mass/charge transport processes, as reported for non-ordered
8 films.^[237] Finally, one has to mention that composite films made of silica in mixture with
9 cation-exchange polymers (such as poly(styrene sulfonate) or Nafion bearing the $\text{Ru}(\text{bpy})_3^{2+}$
10 luminophore) can be also used as ECL sensors,^[238-240] yet exhibiting lower analytical
11 performance compared to the pure silica thin films (Table 1) probably due to slower
12 transport properties. This can be improved somehow by using conducting polymers and/or
13 nanoparticles as additives. A first example is the ECL sensor for codeine phosphate obtained
14 on the basis of a gold electrode modified with a conducting adhesive and a silica film doped
15 with $\text{Ru}(\text{bpy})_3^{2+}$, for which the sensitivity and stability was significantly improved by
16 introducing $\text{nanoTiO}_2\text{-ZnO}$ into the film.^[241] Another one is the ECL sensing of H_2O_2 based
17 on VMSF with immobilized luminol, for which the use of trimethylammonium-
18 functionalized silica mesopores modified with AuNP helps to enhance sensitivity towards
19 H_2O_2 for more than two orders of magnitude compared to a corresponding unfunctionalized
20 film.^[169, 170]

21 So far, the combination of ECL detection with molecular fingerprint recognition
22 remains rare (Table 2). A recent example is the development of an electrochemiluminescent
23 response molecularly imprinted composite film with high affinity for Ochratoxin A (OTA)
24 and good sensitivity owing to the use of suitable additives (Fig. 7B).^[242] For this purpose, a
25 mesoporous SiO_2 film was drop-casted as nanosheets on the surface of graphene oxide (GO)

1 and used as support to load graphene quantum dot (NGQDs) and CsPbBr₃ perovskite
2 nanocrystals (PNCs) (see part B₁ in Fig. 7B). Such special architecture made possible to
3 achieve an efficient self-enhanced ECL reaction between NGQDs and PNCs inside the
4 nanocomposite film (see part B₂ in Fig. 7B), leading to very high sensitivity for OTA
5 sensing with a detection limit as low as 0.2 pg/mL. Moreover, depositing a molecularly
6 imprinted polymer with OTA on top of the composite film, acting as both a protective
7 barrier and a selective recognition layer, made possible the determination of the target OTA
8 analyte with good selectivity over other typical mycotoxins (zearalenone, vomitoxin, and
9 aflatoxins B1 and B2).^[242]

10 A last category is that of ECL biosensors involving usually two critical components:
11 a recognition biomolecule and a luminophore, which are selected for their ability to
12 significantly improve selectivity and sensitivity of detection of the target substrate. Several
13 examples have been reported (Table 4). A screen-printed carbon electrode covered with a
14 first layer of polyluminal (likely to detect H₂O₂ by ECL) and a silica-Nafion overlayer
15 encapsulating choline oxidase was applied to choline biosensing.^[247] The detection principle
16 is the ECL determination of the product of enzymatic transformation of choline (*i.e.*, H₂O₂),
17 the porous structure of the film enabling choline diffusion to the encapsulated enzyme
18 molecules, and the bilayer configuration preventing form luminol leaching.^[248] Other
19 polymer-silica composite films entrapping alcohol dehydrogenase along with Ru(bpy)₃²⁺
20 luminophore were applied to ECL sensing of ethanol in the μM concentration range.^[244, 245]
21 In both cases, the silica network offered a good microenvironment for keeping the biological
22 activity of the entrapped enzymes and the negatively-charged organic polymers improved
23 the binding ability for immobilization of Ru(bpy)₃²⁺ species. A glucose ECL flow-injection
24 biosensor was otherwise developed on the basis of Ru(bpy)₃²⁺-doped mesoporous silica
25 (obtained in the presence of PEG-400 template) and glucose dehydrogenase (GDH)

1 immobilized in polymer Resydrol, as a thin biocomposite film deposited onto a transparent
2 ITO electrode.^[243] NADH, which is produced by the reaction of co-enzyme NAD⁺ and
3 glucose catalyzed by GDH, reacted with immobilized Ru(bpy)₃²⁺ to generate ECL emission.

4 Nanomaterials-based luminophores are a perspective way to enhance sensitivity and
5 selectivity of ECL sensors because they provide excellent signal transduction pathways.
6 They play a significant role in ECL research by essentially functioning as emitters,
7 accelerators, carriers, and multifunctional nanocomponents.^[241-243, 246, 249] This is notably
8 the case of noble metal nanoclusters exhibiting enhanced ECL emission due to the formation
9 of a rigid shell through a host–guest interaction on the metal surface, or other nanomaterials
10 acting as nanocarriers of luminophores for signal amplification (*e.g.*, Au and Ag NPs,
11 magnetic nanoparticles, quantum dots, 2D nanomaterials (such as GO, MXene, and metal–
12 organic layers), nanofibers, nanorods, and silica NPs).^[249] They were also used in ECL
13 biosensors, as exemplified for the ultrasensitive detection of NADH and ethanol using a
14 gold disk electrode modified with partially sulfonated (3-mercaptopropyl)-trimethoxysilane
15 sol–gel bearing Ru(bpy)₃²⁺ species and Au NPs, alone or with the enzyme alcohol
16 dehydrogenase.^[246] The presence of Au NPs enhanced the electron transfer between
17 Ru(bpy)₃²⁺ and the electrode, resulting in the possible determination of these analytes at
18 very low concentration (detection limits of 1 nM for NADH and 12 nM for ethanol).

19 Finally, beside the ECL aptasensor described in section 4.3 involving Ru(bpy)₃²⁺-
20 doped VMSF with adsorbed aptamers (Fig 6A),^[222] a series of geno- and immuno-sensors
21 with ECL detection have been reported (Table 4). In a first example, a glassy carbon
22 electrode modified with a bilayer of mesoporous silica and chitosan bearing luminol,
23 functionalized with human epidermal growth factor receptor 2 (HER-2) antibody, was used
24 for ECL cyto-immunosensing of metastatic breast cancer cells (SKBR-3), which was quite

1 selective in the presence of other interfering cells (such as MCF-7 and MDA-MB-231).^[250]
2 Another recent example is the highly sensitive (femtomolar range) ECL biosensing of a
3 leukaemia marker (BCR/ABL fusion gene detection) using a silica-luminol thin film
4 modified with Au NPs and a ferrocene-labelled molecular beacon (Fc-MB).^[251] Fc-MB
5 served as a catalyst for the luminol ECL reaction which was enhanced by the presence of
6 Au NPs. Upon hybridization with target DNA, ferrocene moieties departed from the
7 nanocomposite electrode surface by stem opening of the Fc-MB reagent, resulting in a
8 decrease in ECL intensity proportional to the probe concentration.

9 **5.2. Other sensors**

10 Beside their use in amperometric/voltammetric devices, silica thin films are
11 considered as prospective membranes for potentiometric sensors or ion-selective field-
12 effect transistors (ISFET) exhibiting high sensitivity and requiring small sample volume.
13 Among the potentiometric sensors, one can cite a carbon paste electrode modified with
14 diazo-thiophenol-functionalized silica for the detection of Ag(I) (with LOD at 9.5×10^{-7}
15 M),^[252] or the selective potentiometric detection of chloride ions using an ultra-thin (300
16 nm thick) nanostructured film of porous silica grafted with amino-groups and gold
17 nanoparticles.^[253] A potentiometric biosensor for urea has been fabricated by immobilizing
18 urease in a composite film made of silica and MWCNTs on ITO electrode, exhibiting a fast
19 response time (10–25 s) with a sensitivity of 23 mV/decade in the concentration range
20 extending from 0.02 to 1 mM.^[254] Knowing that sol-gel films can be patterned on ISFETs
21 by photo-assisted electrodeposition,^[255] or deposited as ultrathin layers on p-type and n-type
22 organic field effect transistors (OFETs) by spin-coating,^[256] and that such films can be
23 generated in the form of composites with organic compounds or polymers,^[257-259] has
24 opened the door to silica-based ISFET and OFET sensors. To name but a few, there are the

1 Si/SiO₂-based ISFETs functionalized with either thiocalix[4]arene for the detection of
2 copper(II) ions^[260] or butyrylcholinesterase for sensing organophosphorus pesticides,^[261] or
3 OFETs silanized with various organosilanes and applied to gas sensing.^[262]

4 Other gas sensors have been developed on the basis of composite silica films, but
5 the silica material acted mostly as a support for the active components and/or as a way to
6 enhance mass transport properties and therefore improving the response time and sensitivity
7 of the devices. Detection was mainly performed by optical methods, quartz crystal
8 microbalance measurements, or resistance monitoring. As this review is devoted to
9 electrochemical sensors, we will only consider the resistive-type gas sensors. Examples are
10 available for hydrogen sensing in the 50-100 ppm concentration range with using Pd-silica
11 thin films exhibiting fast resistance changes (10-30 s),^[263] the room-temperature detection
12 of ammonia gas at ppb level with an Ag-doped γ -Fe₂O₃/SiO₂ composite film,^[264] or gaseous
13 hydrogen sulphide sensing via resistance monitoring of TiO₂/SiO₂ composite aerogel
14 deposited onto gold interdigitated electrodes offering a detection limit of 0.5 ppm at 250°C
15 (with 53 s response time and 74 s recovery time).^[265]

16 Finally, one can also cite the use of Au@SiO₂ core-shell nanoparticles for improving
17 the performance of either electrochemical surface plasmon resonance (SPR) studies^[266] or
18 the detection of molecular species by surface-enhanced Raman spectroscopy (SERS).^[267]
19 Clad-based fiber SPR or local surface plasmon resonance (LSPR) sensors with an additional
20 layer of oxide material including SiO₂ had demonstrated enhanced sensing performance in
21 terms of reliability, sensitivity and long-term stability.^[268, 269] This is because the oxide
22 overlayer enlarged the evanescent field towards the sensing region and protected metal
23 surface from degradation. Silica layer can also act as a linker for modification of such
24 sensors, and the use of these materials is perspective for biosensing.^[268] To date, however,

1 there are only few ‘real’ electrochemical (bio)sensors’ applications based on these systems.
2 One related example is the use of a composite film made of Au NPs, SiO₂ NPs, and graphene
3 oxide, for the electrochemical SPR biosensing of NADH, for which detection can be
4 achieved by both differential pulse voltammetry (DPV) and SPR, yet with an SPR response
5 less sensitive than the DPV one.^[270]

6

7 **6. Conclusion and outlook**

8 Composite materials made of sol-gel-derived silica, being either nanostructured
9 around soft templates, or functionalized with organic moieties, or doped with suitable
10 reagents, macromolecules or nanomaterials, are attractive electrode modifiers for
11 applications in electrochemical sensing and biosensing. This review focused especially on
12 the recent advances made with these composite materials deposited as continuous thin films
13 on electrode surfaces, in relation to their use as promising platforms for electrochemical
14 sensing devices. The versatility of the sol-gel process makes it possible to generate thin
15 films with a wide range of composition and nanoscale organization, including the physical
16 entrapment of conductive or catalytic nano-objects and/or biologically active materials.
17 They can be obtained by evaporation-induced polycondensation or electrochemically
18 assisted deposition. So far, the main electrochemical sensing applications are in the fields
19 of preconcentration electroanalysis, electrocatalytic detection, selective recognition by
20 complexation or molecular imprinting, permselective accumulation/rejection of
21 analytes/interferences, electrochemical enzymatic sensors, geno/apta/immunosensors, and
22 detection by electrogenerated chemiluminescence. A major attractiveness of the silica
23 network relies on its rigidity, imparting a mechanical stability to the porous film, thus
24 enabling easy and fast diffusion of analytes (and reagents) to the electrode surface. This
25 becomes overwhelming for silica frameworks produced in an organized form with

1 mesopore channels of monodisperse diameter all oriented vertically relative to the
2 underlying electrode support, resulting in dramatic increases in sensitivity of the sensors.
3 One can also play with the composite composition and structure to ensure proper selectivity
4 to the sensors. Another major interest is the possibility to immobilize redox proteins and
5 enzymes by sol-gel bioencapsulation while keeping their biological activity and the
6 accessibility to their substrates and cofactors, leading to good performance electrochemical
7 biosensing. A drawback of silica materials when used for electrochemical purposes is their
8 insulating properties, but this can be solved somehow by associating metal nanoparticles,
9 conducting polymers or nanocarbons, or by attaching redox moieties likely to enable charge
10 transfer by electron hopping. These additives can otherwise contribute to induce more
11 effective electrocatalytic properties. However, a major practical constraint of silica gel is its
12 rather poor chemical stability in solution, especially when rising pH, which may lead to
13 limited long-term operational stability of silica-based electrochemical sensors and
14 biosensors.

15 Among the first prospects in this field, it is therefore not surprising to affirm the
16 need to improve the chemical stability of composite films in order to increase the long-term
17 operational use of electrochemical devices integrating composite silica-based thin films. A
18 possible direction would be the formation of silica-based mixed oxide films (*e.g.*,
19 mesoporous silica films prepared with 10% or less ZrO₂ or Al₂O₃ undergo much less
20 degradation than pure silica materials under biologically relevant conditions^[271]) for which
21 significant improvement in chemical stability under electrochemical cycling can be
22 observed.^[272] Even more stable oxide films can be obtained (*e.g.*, IrO_x nanostructures
23 prepared using VMSF as hard template and used for pH sensing at human skin surface,^[273]
24 yet after dissolution of the silica membrane), but they are losing one key advantage of silica-
25 based materials: the possibility to be derivatized with organo-functional groups. And such

1 functionalization to get organic-inorganic composite films constitutes another attractive
2 perspective in the field, not only to improve their chemical stability,^[274, 275] but also to create
3 novel properties and additional reactivity towards the target analytes. In particular, the
4 possibility of obtaining multifunctional mesoporous thin films by combining several
5 selective click reactions,^[63] or by functionalization strategies likely to achieve a spatial
6 surface modification or selective deposition of guest species within multimodal and
7 hierarchical ordered mesoporous materials.^[276] The achievement of multiple
8 functionalization and extending the possibilities of host-guest interactions in designing
9 silica-based composite thin films should also contribute to explore new horizons and to
10 bring real synergetic (and not only additional) effects expected to improve the analytical
11 performance of the electrochemical (bio)sensors in terms of enhanced sensitivity, selectivity
12 and stability. Finally, the emergence of 3D-printing technologies starts to benefit
13 electrochemistry,^[277] in particular for manufacturing electrochemical sensors,^[278, 279] but
14 this has not yet been exploited in connection to composite silica-based thin films.
15 Considering that 3D-printed conductive materials can be produced as porous electrodes of
16 complex geometry,^[280] such new generation electrodes could be easily modified with silica-
17 based thin films prepared by electrochemically assisted deposition, in the same way as that
18 applied to uniformly coat the inner surface of macroporous metal electrodes with sol-gel
19 biocomposites^[34] or to generate vertically aligned mesoporous silica films on 3D graphene-
20 carbon nanotube assemblies,^[149] for instance. Another strategy could be the direct additive
21 manufacturing of composite electrodes made of a conductive matrix (carbon, metal) and
22 silica with a mesoporous structure (the 3D-printing of ordered mesoporous silica monoliths
23 has been developed,^[281] and it could be extended to the production of conductive
24 nanocomposites). This would offer novel nanofabrication opportunities especially attractive
25 for miniaturization of the composite silica-based electrochemical sensors.

26

1 **7. References**

- 2 [1] J. Fraden, *Handbook of Modern Sensors*, Springer, Cham. **2016**, pp. 645-697.
- 3 [2] H Ju, J. Li (eds), *Biochemical Sensors, vol. 1 Fundament and Development*, World
4 Scientific Series (From Biomaterials Towards Medical Devices, vol. 4), Singapore, **2021**.
- 5 [3] D. Yang, in: B. S. R. Reddy (ed), *Advances in Nanocomposites – Synthesis,*
6 *Characterization and Industrial Applications*, InTech Open, Rijeka, Croatia, **2011**, chap.
7 37, pp. 857–882.
- 8 [4] V. P. Elanjeitsenni, K. S. Vadivu, B. M. Prasanth, *Mater. Res. Express* **2022**, 9, 022001.
- 9 [5] T. Ribeiro, C. Baleizão, J. P. S. Farinha, *Materials* **2014**, 7, 3881–3900.
- 10 [6] B. Barsan, G. Gauglitz, A. Oprea, E. Ostertag, G. Proll, K. Rebner, K. Schierbaum,
11 *Chemical and Biochemical Sensors, 1. Fundamentals*, Wiley-VCH, Weinheim, **2016**.
- 12 [7] J. Wang, *Anal. Chim. Acta* **1999**, 399, 21–27.
- 13 [8] A. Walcarius, *Chem. Mater.* **2001**, 13, 3351–3372.
- 14 [9] L. Rabinovich, O. Lev, *Electroanalysis* **2001**, 13, 265–275.
- 15 [10] A. Walcarius, *Electroanalysis* **2001**, 13, 701–718.
- 16 [11] Y. Gushikem, S. S. Rosatto, *J. Braz. Chem. Soc.* **2001**, 12, 695–705.
- 17 [12] S. V. Aurobind, K. P. Amirthalingam, H. Gomathi, *Adv. Colloid Interface Sci.* **2006**,
18 121, 1–7.
- 19 [13] K. Miecznikowski, J. A. Cox, *J. Solid State Electrochem.* **2020**, 24, 2617–2631.

- 1 [14] A. Walcarius, D. Mandler, J. Cox, M. M. Collinson, O. Lev, *J. Mater. Chem.* **2005**, *15*,
2 3663–3689.
- 3 [15] A. Walcarius, A. Kuhn, *Trends Anal. Chem.* **2008**, *27*, 593–603.
- 4 [16] A. Walcarius, *Electroanalysis* **2015**, *27*, 1303–1340.
- 5 [17] O. Lev, Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich, S.
6 Sampath, *Chem. Mater.* **1997**, *9*, 2354–2375.
- 7 [18] J. Wen, G. L. Wilkes, *Chem. Mater.* **1996**, *8*, 1667–1681.
- 8 [19] C. Sanchez, F. Ribot, B. Lebeau, *J. Mater. Chem.* **1999**, *9*, 35–44.
- 9 [20] O. Lev, D. Rizkov, S. Mizrahi, I. Ekeltchik, Z. G. Kipervaser, V. Gitis, A. Goifman,
10 D. Tessema, A. Kamyshny Jr., A. Modestov, J. Gun, in: L. Klein, M. Aparicio, A. Jitianu
11 (eds), *Handbook of Sol-Gel Science and Technology*, Springer, Cham, **2018**, pp. 2663–2694.
- 12 [21] M. Faustini, L. Nicole, E. Ruiz-Hitzky, C. Sanchez, *Adv. Funct. Mater.* **2018**, *28*,
13 1704158.
- 14 [22] S. N. Tan, W. Wang, L. Ge, in: P. Ducheyne (ed.), *Comprehensive Biomaterials II*,
15 Elsevier, Oxford, 2017, vol. 3, p. 657–689.
- 16 [23] P. Innocenzi, *Chem. Sci.* **2022**, *13*, 13264–13279.
- 17 [24] M. Etienne, A. Quach, D. Grosso, L. Nicole, C. Sanchez, A. Walcarius, *Chem. Mater.*
18 **2007**, *19*, 844–856.
- 19 [25] A. Walcarius, *Chem. Soc. Rev.* **2013**, *42*, 4098–4140.
- 20 [26] A. Walcarius, *Acc. Chem. Res.* **2021**, *54*, 3563–3575.

- 1 [27] P. Zhou, L. Yao, K. Chen, B. Su, *Crit. Rev. Anal. Chem.* **2020**, *50*, 424–444.
- 2 [28] A. Walcarius, *Electroanalysis* **2008**, *20*, 711–738.
- 3 [29] A. Walcarius, P. Audebert, in: P. Gomez-Romero, C. Sanchez (eds.), *Functional*
4 *Hybrid Materials*, Wiley-VCH, Weinheim, **2004**, Chap. 6, pp. 172–209.
- 5 [30] C.J. Brinker, G.W. Scherer, *Sol-Gel Science*, Academic Press, San Diego, **1990**.
- 6 [31] C.J. Brinker, A.J. Hurd, P.R. Schunk, G.C. Frye, C.S. Ashley, *J. Non-Cryst. Solids*
7 **1992**, *147-148*, 424–436.
- 8 [32] M.M. Collinson, *Acc. Chem. Res.* **2007**, *40*, 777–783.
- 9 [33] L. Liu, D. Mandler, in: L. Klein, M. Aparicio, A. Jitianu (eds.), *Handbook of Sol-Gel*
10 *Science and Technology*, Springer, Cham, **2018**, pp. 531-568.
- 11 [34] F. Qu, R. Nasraoui, M. Etienne, Y. Bon Saint Come, A. Kuhn, J. Lenz, J. Gajdzik, R.
12 Hempelmann, A. Walcarius, *Electrochem. Commun.* **2011**, *13*, 138–142.
- 13 [35] I. Mazurenko, M. Etienne, R. Ostermann, B. M. Smarsly, O. Tananaiko, V. Zaitsev, A.
14 Walcarius, *Langmuir* **2011**, *27*, 7140–7147.
- 15 [36] J. Wang, N. Vilà, A. Walcarius, *Electrochim. Acta* **2021**, *366*, 137407.
- 16 [37] I. Mazurenko, M. Etienne, O. Tananaiko, V. Zaitsev, A. Walcarius, *Electrochim. Acta*
17 **2012**, *83*, 359–366.
- 18 [38] E. Sibottier, S. Sayen, F. Gaboriaud, A. Walcarius, *Langmuir* **2006**, *22*, 8366–8373.
- 19 [39] X. Wang, N. Ben Ahmed, G. S. Alvarez, M. V. Tuttolomondo, C. Hélyary, M. F.
20 Desimone, T. Coradin, *Curr. Top. Med. Chem.* **2015**, *15*, 223–244.

- 1 [40] O. Nadzhafova, M. Etienne, A. Walcarius, *Electrochem. Commun.* **2007**, *9*, 1189–
2 1195.
- 3 [41] W.-Z. Jia, K. Wang, Z.-J. Zhu, H.-T. Song, X.-H. Xia, *Langmuir* **2007**, *23*, 11896–
4 11900.
- 5 [42] W. Ghach, M. Etienne, P. Billard, F. Jorand, A. Walcarius, *J. Mater. Chem. B* **2013**, *1*,
6 1052–1059.
- 7 [43] W. Boumya, S. Charafi, M. Achak, H. Bessbousse, A. Elhalil, M. Abdennouri, N.
8 Barka, *Res. Chem.* **2022**, *4*, 100623.
- 9 [44] X. Liu, B. Li, X. Wang, C. Li, *Microchim. Acta* **2010**, *171*, 399–405.
- 10 [45] G. Arken, G. Li, X. Zheng, X. Liu, *Anal. Lett.* **2014**, *47*, 2522–2536.
- 11 [46] A. Kovalyk, O. Tananaiko, A. Borets, M. Etienne, A. Walcarius, *Electrochim. Acta*
12 **2019**, *306*, 680–687.
- 13 [47] L. Fang, Q.-Q. He, M.-J., Zhou, J.-P. Zhao, *Electrochem. Commun.* **2019**, *109*, 106609.
- 14 [48] X. Q. Du, Y. W. Liu, D. C. Chen, Z. Zhang, Y. Chen, *Surf. Coat. Technol.* **2022**, *436*,
15 128279.
- 16 [49] D. Ravi Shankaran, N. Ueheara, T. Kato, *Biosens. Bioelectron.* **2003**, *18*, 721–728.
- 17 [50] M. Yang, Y. Yang, Y. Liu, G. Shen, R. Yu, *Biosens. Bioelectron.* **2006**, *21*, 1125–1131.
- 18 [51] L. Lei, Z. Cao, Q. Xie, Y. Fu, Y. Tan, M. Ma, S. Ya, *Sens. Actuat. B* **2011**, *157*, 282–
19 289.
- 20 [52] M. Raveh, L. Liu, D. Mandler, *Phys. Chem. Chem. Phys.* **2013**, *15*, 10876–10884.

- 1 [53] T.-C. Wei, H. W. Hillhouse, *Langmuir* **2007**, *23*, 5689–5699.
- 2 [54] M. Etienne, Y. Guillemain, D. Grosso, A. Walcarius, *Anal. Bioanal. Chem.* **2013**, *405*,
3 1497–1512.
- 4 [55] L. Rimoldi, V. Pifferi, D. Meroni, G. Soliveri, S. Ardizzone, L. Falciola, *Electrochim.*
5 *Acta* **2018**, *291*, 73–83.
- 6 [56] S. Sayen, M. Etienne, J. Bessière, A. Walcarius, *Electroanalysis* **2002**, *14*, 1521–1525.
- 7 [57] M. Etienne, A. Walcarius, *Electrochem. Commun.* **2005**, *7*, 1449–1456.
- 8 [58] C. Sanchez, C. Boissière, D. Grosso, C; Laberty, L. Nicole, *Chem. Mater.* **2008**, *20*,
9 682–737.
- 10 [59] D. Feng, J. Wei, M. Wang, Q. Yue, Y. Deng, A.M. Asiri, D. Zhao, *Adv. Porous Mater.*
11 **2013**, *1*, 164–186.
- 12 [60] A. Walcarius, E. Sibottier, M. Etienne, J. Ghanbaja, *Nature Mater.* **2007**, *6*, 602–608.
- 13 [61] A. Goux, M. Etienne, E. Aubert, C. Lecomte, J. Ghanbaja, A. Walcarius, *Chem. Mater.*
14 **2009**, *21*, 731–741.
- 15 [62] G. E. Moehl, T. Nasir, Y. Han, Y. J. Noori, R. Huang, R. Beanland, P. N. Bartlett, A.
16 L. Hector, *Nanoscale* **2022**, *14*, 5404–5411.
- 17 [63] N. Vilà, J. Ghanbaja, E. Aubert, A. Walcarius, *Angew. Chem. Int. Ed.* **2014**, *53*, 2945–
18 2950.
- 19 [64] N. Vilà, J. Ghanbaja, A. Walcarius, *Adv. Mater. Interfaces* **2016**, *3*, 1500440.
- 20 [65] N. Vilà, A. Walcarius, *Electrochim. Acta* **2015**, *179*, 304–314.

- 1 [66] Z. Teng, G. Zheng, Y. Dou, W. Li, C.-Y. Mou, X. Zhang, A. M. Asiri, D. Zhao, *Angew. Chem. Int. Ed.* **2012**, *51*, 2173–2177.
- 2
- 3 [67] M.-A. Pizzoccaro-Zilamy, C. Huiskes, E. G. Keim, S. N. Sluijter, H. van Veen, A. Nijmeijer, L. Winnubst, and M. W. J. Luiten-Olieman, *ACS Appl. Mater. Interfaces* **2019**,
- 4 *11*, 18528–18539.
- 5
- 6 [68] X. Lin, Q. Yang, L. Ding, B. Su, *ACS Nano* **2015**, *9*, 11266–11277.
- 7
- 8 [69] C. Karman, N. Vilà, A. Walcarius, *ChemElectroChem* **2016**, *3*, 2130–2137.
- 9
- 10 [70] N. Vilà, E. André, R. Ciganda, J. Ruiz, D. Astruc, A. Walcarius, *Chem. Mater.* **2016**,
- 11 *28*, 2511–2514.
- 12
- 13 [71] W. Yantasee, B. Charnhattakorn, G. E. Fryxell, Y. Lin, C. Timchalk, R. S. Addleman, *Anal. Chim. Acta* **2008**, *620*, 55–63.
- 14
- 15 [72] I. Sebarchievici, B.-O. Taranu, S.F. Rus, E. Fagadar-Cosma, *J. Electroanal. Chem.* **2020**, *865*, 114127.
- 16
- 17 [73] A. Kornii, V. V. Lisnyak, L. Grishchenko, O. Tananaiko, *Electrochim. Acta* **2022**, *409*,
- 18 *139938*.
- 19
- 20 [74] N. Shaabani, N. W. C. Chan, A. B. Jemere, *Nanomaterials* **2021**, *11*, 631.
- [75] O. Yu. Nadzhafova, T. S. Rozhanchuk, V. N. Zaitsev, V. V. Shevchenko, *Ukr. Chim. Zhurn.* **2008**, *74*, 59–64.
- [76] P.-G. Su, W.-L. Shiu, M.-S. Tsai, *Sens. Actuat. B* **2015**, *216*, 467–475.
- [77] S. Zuo, Y. Teng, H. Yuan, M. Lan, *Sens. Actuat. B* **2008**, *133*, 555–560.

- 1 [78] C. T. Canevari, P. A. Raymundo-Pereira, R. Landers, E. V. Benvenuti, S. A. S.
2 Machado, *Talanta* **2013**, *116*, 726–735.
- 3 [79] K. M. Wiaderek, J. A. Cox, *Electrochim. Acta* **2011**, *56*, 3537–3542.
- 4 [80] G. Maduraiveeran, P. Manivasakan, R. Ramaraj, *Int. J. Nanotechnol.* **2011**, *8*, 925–
5 934.
- 6 [81] P. Yang, H. Cai, S. Liu, Q. Wan, X. Wang, N. Yang, *Electrochim. Acta* **2011**, *56*, 7097–
7 7103.
- 8 [82] P. L. Almeida Jr., C. H. S. Mendes, I. A. F. S. Lima, M. F. Belian, S. C. B. Oliveira, C.
9 M. A. Brett, V. B. Nascimento, *Anal. Lett.* **2018**, *51*, 496–511.
- 10 [83] S. Bharathi, M. Nogami, O. Lev, *Langmuir* **2001**, *17*, 2602–2609.
- 11 [84] A. Celebanska, M. Opalio, *ChemElectroChem* **2016**, *3*, 1629–1634.
- 12 [85] G. Maduraiveeran, R. Ramaraj, *J. Electroanal. Chem.* **2007**, *608*, 52–58.
- 13 [86] X. Liu, L. Xie, H. Li, *J. Electroanal. Chem.* **2012**, *682*, 158–163.
- 14 [87] A. Taheri, M. Noroozifar, M. Khorasani-Motlagh, *J. Electroanal. Chem.* **2009**, *628*,
15 48–54.
- 16 [88] I. Sadok, K. Tyszczyk-Rotko, *J. Electroanal. Chem.* **2018**, *808*, 204–210.
- 17 [89] Y. Battie, O. Ducloux, L. Patout, P. Thobois, A. Loiseau, *Sens. Actuat. B* **2012**, *163*,
18 121–127.
- 19 [90] A. Hassan Oghli, A. Soleymanpour, *Microchem. J.* **2022**, *173*, 107034.

- 1 [91] S. Kozhukharova, Z. Nenova, T. Nenov, N. Nedev, M. Machkova, *Sens. Actuat. B* **2015**,
2 *210*, 676–684.
- 3 [92] E. L. Holthoff, F. V. Bright, *Anal. Chim. Acta* **2007**, *594*, 147–161.
- 4 [93] C. G. Xie, B. H. Liu, Z. Y. Wang, D. M. Gao, G. J. Guan, Z. P. Zhang, *Anal. Chem.*
5 **2008**, *80*, 437–443.
- 6 [94] B. B. Prasad, R. Madhuri, M. P. Tiwari, P. S. Sharma. *Biosens. Bioelectron.* **2010**, *25*,
7 2140–2148.
- 8 [95] J. Zhang, Y. Q. Wang, R. H. Lv, L. Xu, *Electrochim. Acta* **2010**, *55*, 4039–4044.
- 9 [96] T. Sikolenko, E. Bou-Maroun, T. Karbowskiak, *Curr. Opin. Electrochem.* **2022**, *36*,
10 101151.
- 11 [97] R. Makote, M.M. Collinson, *Chem. Mater.* **1998**, *10*, 2440–2445.
- 12 [98] N. F. Atta, A. M. Abdel-Mageed, *Talanta* **2009**, *80*, 511–518.
- 13 [99] T. Rozhanchuk, M. Velychko, M. Titov, O. Tananaiko, *Electroanalysis* **2013**, *25*,
14 2045–2053.
- 15 [100] J. Luo, J. Cong, R. Fang, X. Fei, X. Liu, *Microchim. Acta* **2014**, *181*, 1257–1266.
- 16 [101] Z. Zhang, Y. Hu, H. Zhang, L. Luo, S. Yao, *Biosens. Bioelectron.* **2010**, *26*, 696–702.
- 17 [102] W. de J. R. Santos, M. Santhiago, I. V. P. Yoshida, L. T. Kubota, *Anal. Chim. Acta*
18 **2011**, *695*, 44–50.
- 19 [103] W. J. R. Santos, M. Santhiago, I. V. P. Yoshida, L. T. Kubota, *Sens. Actuat. B* **2012**,
20 *166–167*, 739–745.

- 1 [104] Y. Hu, J. Li, Z. Zhang, H. Zhang, L. Luo, S. Yao, *Anal. Chim. Acta* **2011**, *698*, 61–
2 68.
- 3 [105] J. Huang, X. Zhang, Q. Lin, X. He, X. Xing, H. Huai, W. Lian, H. Zhu, *Food Control*
4 **2011**, *22*, 786-791.
- 5 [106] Y.-F. Hu, Z.-H. Zhang, H.-B. Zhang, L.-J. Luo, S.-Z. Yao, *Talanta* **2011**, *84*, 305–
6 313.
- 7 [107] Z. Zhang, Y. Hu, H. Zhang, L. Luo, S. Yao, *J. Electroanal. Chem.* **2010**, *644*, 7–12.
- 8 [108] C. Lafarge, M. Bitar, L. El Hosry, P. Cayot, E. Bou-Maroun, *Mater. Today Commun.*
9 **2020**, *24*, 101157.
- 10 [109] X. Tan, B. Li, K. Y. Liew, C. Li, *Biosens. Bioelectron.* **2010**, *26*, 868–871.
- 11 [110] S. Fireman-Shoresh, I. Turyan, D. Mandler, S. Marx, *Langmuir* **2005**, *21*, 7842–7847.
- 12 [111] J. Zou, G.-Q. Zhao, G.-L. Zhao, J.-G. Yu, *Coord. Chem. Rev.* **2022**, *471*, 214732.
- 13 [112] S. Zhu, X. Lin, Q. Wang, Q. Xia, P. Ran, Y. Fu, *Electroanalysis* **2017**, *29*, 466–471.
- 14 [113] I. Sulym, A. Cetinkaya, M. Yence, M. E. Çorman, L. Uzun, S. A. Ozkan, *Electrochim.*
15 *Acta* **2022**, *430*, 141102.
- 16 [114] S. Li, D. Du, J. Huang, H. Tu, Y. Yang, A. Zhang, *Analyst* **2013**, *138*, 2761–2768.
- 17 [115] H. Zhou, Y. Ding, R. Su, D. Lu, H. Tang, F. Xi, *Front. Chem.* **2022**, *9*, 812086.
- 18 [116] M. Etienne, J. Cortot, A. Walcarius, *Electroanalysis* **2007**, *19*, 129–138.
- 19 [117] A. Jieumboué Tchinda, E. Ngameni, A. Walcarius, *Sens. Actuat. B* **2007**, *121*, 113–
20 123.

- 1 [118] A. Sanchez, A. Walcarius, *Electrochim. Acta* **2010**, *55*, 4201–4207.
- 2 [119] W. Yantasee, Y. Lin, X. Li, G. E. Fryxell, T. S. Zemanian, V. V. Viswanathan, *Analyst*
3 **2003**, *128*, 899-904.
- 4 [120] Z. Li, H. Xu, D. Wu, J. Zhang, X. Liu, S. Gao, Y. Kong, *ACS Appl. Mater. Interfaces*
5 **2019**, *11*, 2840–2848.
- 6 [121] F. Xi, L. Xuan, L. Lu, J. Huang, F. Yan, J. Liu, X. Dong, P. Chen, *Sens. Actuat. B*
7 **2019**, *288*, 133–140.
- 8 [122] M. Saadaoui, I. Fernández, A. Sánchez, P. Díez, S. Campuzano, N. Raouafi, J. M.
9 Pingarrón, R. Villalonga, *Electrochem. Commun.* **2015**, *58*, 57–61.
- 10 [123] F. Yan, M. Wang, Q. Jin, H. Zhou, L. Xi, H. Tang, J. Liu, *J. Electroanal. Chem.* **2021**,
11 *881*, 114969.
- 12 [124] Y. Zou, X. Zhou, L. Xie, H. Tang, F. Yan, *Front. Chem.* **2022**, *10*, 939510.
- 13 [125] F. Yan, T. Luo; Q. Jin, H. Zhou, A. Sailjoi, G. Dong, J. Liu, W. Tang, *J. Hazard.*
14 *Mater.* **2021**, *410*, 124636.
- 15 [126] J. Huang, T. Zhang, Y. Zheng, J. Liu, *Biosensors* **2023**, *13*, 317.
- 16 [127] J. Gong, T. Zhang, P. Chen, F. Yan, J. Liu, *Sens. Actuat. B* **2022**, *368*, 132086.
- 17 [128] Q. Han, T. Zhang, M. Wang, F. Yan, J. Liu, *Molecules* **2022**, *27*, 8200.
- 18 [129] X. Wei, X. Luo, S. Xu, F. Xi, T. Zhao, *Front. Chem.* **2022**, *10*, 872582.
- 19 [130] K. Wang, L. Yang, H. Huang, N. Lv, J. Liu, Y. Liu, *Molecules* **2022**, *27*, 2739.
- 20 [131] N. Ma, X. Luo, W. Wu, J. Liu, *Nanomater.* **2022**, *12*, 3981.

- 1 [132] A. Maghear, M. Etienne, M. Tertiş, R. Sandulescu, A. Walcarius, *Electrochim. Acta*
2 **2013**, *112*, 333–341.
- 3 [133] M. Etienne, A. Goux, E. Sibottier, A. Walcarius, *J. Nanosci. Nanotechnol.* **2009**, *9*,
4 2398–2406.
- 5 [134] H. Maheshwari, N. Vilà, G. Herzog, A. Walcarius, *ChemElectroChem* **2020**, *7*, 2095–
6 2101.
- 7 [135] S. L. Z. Jiokeng, I. K. Tonlé, A. Walcarius, *Sens. Actuat. B* **2019**, *287*, 296–305.
- 8 [136] M. Saadaoui, I. Fernández, G. Luna, P. Díez, S. Campuzano, N. Raouafi, A. Sánchez,
9 J. M. Pingarrón, R. Villalonga, *Anal. Bioanal. Chem.* **2016**, *408*, 7321–7327.
- 10 [137] W. Li, L. Ding, Q. Wang, B. Su, *Analyst* **2014**, *139*, 3926–3931.
- 11 [138] F. Yan, J. Chen, Q. Jin, H. Zhou, A. Sailjoi, J. Liu, W. Tang, *J. Mater. Chem. C* **2020**,
12 *8*, 7113–7119.
- 13 [139] L. Yang, T. Zhang, H. Zhou, F. Yan, Y. Liu, *Front. Nutr.* **2022**, *9*, 987442.
- 14 [140] A. Goux, J. Ghanbaja, A. Walcarius, *J. Mater. Sci.* **2009**, *44*, 6601–6607.
- 15 [141] S. Ahoulou, N. Vilà, S. Pillet, D. Schaniel, A. Walcarius, *Electroanalysis* **2020**, *32*,
16 690–697.
- 17 [142] J. Guo, X. Liu, A. Wang, X. Yu, L. Ding, *Microchem. J.* **2022**, *183*, 107964.
- 18 [143] F. Asadpour, M. Mazloum-Ardakani, F. Hoseynidokht, S. M. Moshtaghioun, *Biosens.*
19 *Bioelectron.* **2021**, *180*, 113124.

- 1 [144] T. Nasir, A. Gamero-Quijano, C. Despas, M. Dossot, G. Herzog, A. Walcarius,
2 *Talanta* **2020**, *220*, 121347.
- 3 [145] R. Liang, J. Jiang, Y. Zheng, A. Sailjoi, J. Chen, J. Liu, H. Li, *RSC Adv.* **2021**, *11*,
4 34669–34675.
- 5 [146] X. Deng, X. Lin, H. Zhou, J. Liu, H. Tang, *Nanomater.* **2023**, *13*, 239.
- 6 [147] C. Karman, N. Vilà, C. Despas, A. Walcarius, *Electrochim. Acta* **2017**, *228*, 659–666.
- 7 [148] T. Nasir, G. Herzog, L. Liu, M. Hébrant, C. Despas, A. Walcarius, *ACS Sensors* **2018**,
8 *3*, 484–493.
- 9 [149] W. Zheng, R. Su, G. Yu, L. Liu, F. Yan, *Nanomater.* **2022**, *12*, 3632.
- 10 [150] L. Yan, S. Xu, F. Xi, *Nanomater.* **2022**, *12*, 3810.
- 11 [151] K. Ma, Y. Zheng, L. An, J. Liu, *Front. Chem.* **2022**, *10*, 851178.
- 12 [152] W. Argoubi, A. Sánchez, C. Parrado, N. Raouafia, R. Villalonga, *Sens. Actuat. B*
13 **2018**, *255*, 309–315.
- 14 [153] Y. Ma, W. Liao, H. Zhou, Y. Tong, J. Liu, F. Yan, H. Tang, J. Liu, *J. Mater. Chem.*
15 *B* **2020**, *8*, 10630–10636.
- 16 [154] H. Zhu, X. Ma, A. Sailjoi, Y. Zou, X. Lin, F. Yan, B. Su, J. Liu, *Sens. Actuat. B* **2022**,
17 *353*, 131101.
- 18 [155] W. Zheng, R. Su, X. Lin, J. Liu, *Front. Chem.* **2022**, *10*, 954802.
- 19 [156] X. Zhu, L. Xuan, J. Gong, J. Liu, X. Wang, F. Xi, *Talanta* **2022**, *238*, 123027.
- 20 [157] K. Ma, L. Yang, J. Liu, J. Liu, *Nanomater.* **2022**, *12*, 1157.

- 1 [158] L. Ding, W. Li, Q. Wang, Q. Sun, S. He, B. Su, *Chem. Eur. J.* **2014**, *20*, 1829–1833.
- 2 [159] L. Ding, W. Li, Q. Sun, S. He, B. Su, *Chem. Eur. J.* **2014**, *20*, 12777–12780.
- 3 [160] J. Wang, J. Yu, Y. Yu, Z. Luo, G. Li, X. Lin, *Food Chem.* **2023**, *405*, 134806.
- 4 [161] X. Mi, H. Li, R. Tan, Y. Tu, *Anal. Chem.* **2020**, *92*, 14640–14647.
- 5 [162] S. Chen, Y. Lei, J. Xu, Y. Yang, Y. Dong, Y. Li, H. Yi, Y. Liao, L. Chen, Y. Xiao,
6 *RSC Adv.* **2022**, *12*, 17330–17336.
- 7 [163] Q. Sun, F. Yan, L. Yao, B. Su, *Anal. Chem.* **2016**, *88*, 8364–8368.
- 8 [164] W. Zheng, B. Su, *J. Electroanal. Chem.* **2016**, *781*, 383–388.
- 9 [165] L. Zhu, W. Fu, J. Chen, S. Li, X. Xie, Z. Zhang, J. Liu, L. Zhou, B. Su, X. Chen, *Sens.*
10 *Actuat. B* **2022**, *366*, 131972.
- 11 [166] F. Yan, X. Ma, Q. Jin, Y. Tong, H. Tang, X. Lin, J. Liu, *Microchim. Acta* **2020**, *187*,
12 470.
- 13 [167] J. Ding, X. Li, L. Zhou, R. Yang, F. Yan, B. Su, *J. Mater. Chem. B* **2020**, *8*, 3616–
14 3622.
- 15 [168] L. Ding, B. Su, *J. Electroanal. Chem.* **2015**, *736*, 83–87.
- 16 [169] J. Zhang, H. Ding, L. Zhu, S. Zhao, D. Jiang, H.-Y. Chen, *Electrochem. Commun.*
17 **2019**, *98*, 38–42.
- 18 [170] Z.-M. Lyu, X.-L. Zhou, X.-N. Wang, P. Li, L. Xu, E.-H. Liu, *Sens. Actuat. B* **2019**,
19 *284*, 437–443.
- 20 [171] Y. Xiao, L. Xu, P. Li, X.-C. Tang, L.-W. Qi, *Anal. Chim. Acta* **2017**, *983*, 96–102.

- 1 [172] Y. Xiao, S. Chen, G. Zhang, Z. Li, H. Xiao, C. Chen, C. He, R. Zhang, X. Yang,
2 *Analyst* **2020**, *145*, 4806–4814.
- 3 [173] L. Yao, F. Yan, B. Su, *Analyst* **2016**, *141*, 2303–2307.
- 4 [174] X. Lin, B. Zhang, Q. Yang, F. Yan, X. Hua, B. Su, *Anal. Chem.* **2016**, *88*, 7821–7827.
- 5 [175] F. Yan, H. He, L. Ding, B. Su, *Anal. Chem.* **2015**, *87*, 4436–4441.
- 6 [176] L. Shi, F. Cao, L. Zhang, Y. Tian, *Anal. Chem.* **2020**, *92*, 4535–4540.
- 7 [177] F. Yan, B. Su, *Anal. Chem.* **2016**, *88*, 11001–11006.
- 8 [178] Q. Sun, F. Yan, B. Su, *Biosens. Bioelectron.* **2018**, *105*, 129–136.
- 9 [179] S. Li, D. Zhang, J. Liu, C. Cheng, L. Zhu, C. Li, Y. Lu, S. S. Low, B. Su, Q. Liu,
10 *Biosens. Bioelectron.* **2019**, *129*, 284–291.
- 11 [180] Z. Zhou, W. Guo, L. Xu, Q. Yang, B. Su, *Anal. Chim. Acta* **2015**, *886*, 48–55.
- 12 [181] L. Lu, L. Zhou, J. Chen, F. Yan, J. Liu, X. Dong, F. Xi, P. Chen, *ACS Nano* **2018**, *12*,
13 12673–12681.
- 14 [182] X. Li, L. Zhou, J. Ding, L. Sun, B. Su, *ChemElectroChem* **2020**, *7*, 2081–2086.
- 15 [183] S. Ahoulou, N. Vilà, S. Pillet, D. Schaniel, A. Walcarius, *Chem. Mater.* **2019**, *31*,
16 5796–5807.
- 17 [184] F. Yan, X. Lin, B. Su, *Analyst* **2016**, *141*, 3482–3495.
- 18 [185] N. Vilà, P. de Oliveira, A. Walcarius, I. M. Mbomekallé, *Electrochim. Acta* **2019**,
19 *309*, 209–218.

- 1 [186] T. Nasir, L. Zhang, N. Vila, G. Herzog, A. Walcarius, *Langmuir* **2016**, *32*, 4323–
2 4332.
- 3 [187] W. Ullah, G. Herzog, N. Vilà, M. Brites-Helu, A. Walcarius, *ChemElectroChem*
4 **2021**, *8*, 142–150.
- 5 [188] L. Xuan, W. Liao, M. Wang, H. Zhou, Y. Ding, F. Yan, J. Liu, H. Tang, F. Xi,
6 *Talanta* **2021**, *225*, 122066.
- 7 [189] M. B. Serrano, C. Despas, G. Herzog, A. Walcarius, *Electrochem. Commun.* **2015**,
8 *53*, 34–36.
- 9 [190] J. Liu, H. Cheng, D. He, X. He, K. Wang, Q. Liu, S. Zhao, X. Yang, *Anal. Chem.*
10 **2017**, *89*, 9062–9068.
- 11 [191] A. Walcarius, M. Etienne, B. Lebeau, *Chem. Mater.* **2003**, *15*, 2161–2173.
- 12 [192] A. Walcarius, C. Delacôte, *Chem. Mater.* **2003**, *15*, 4181–4192.
- 13 [193] A. Walcarius, M. Etienne, S. Sayen, B. Lebeau, *Electroanalysis* **2003**, *15*, 414–421.
- 14 [194] N. Vilà, A. Walcarius, *Front. Chem.* **2020**, *8*, 830.
- 15 [195] S. Ahoulou, N. Vilà, S. Pillet, C. Carteret, D. Schaniel A. Walcarius,
16 *ChemPhysChem* **2021**, *22*, 2464–2477.
- 17 [196] P. Audebert, N. Vilà, C. Allain, F. Maisonneuve, A. Walcarius, P. Hapiot,
18 *ChemElectroChem* **2015**, *2*, 1695–1698.
- 19 [197] M. Etienne, L. Zhang, N. Vilà, A. Walcarius, *Electroanalysis* **2015**, *27*, 2028–2054.

- 1 [198] W. Ullah, G. Herzog, N. Vilà, A. Walcarius, *Electrochem. Commun.* **2021**, *122*,
2 106896.
- 3 [199] A. Gamero-Quijano, C. Karman, N. Vilà, G. Herzog, A. Walcarius, *Langmuir* **33**
4 (2017) 4224–4234.
- 5 [200] A. Walcarius, *Curr. Opin. Electrochem.* **2018**, *10*, 88–97.
- 6 [201] E. Casero, M. D. Petit-Domínguez, L. Vázquez, Enzymatic Sol–Gel Biosensors. In:
7 Klein, L., Aparicio, M., Jitianu, A. (eds), *Handbook of sol-gel science and technology*.-
8 2016.- Springer: Cham. pp. 1-39.
- 9 [202] J. Wang, *Microchim. Acta* **2012**, *177*, 245–270.
- 10 [203] M. U. Anu Prathap, B. Kaur, R. Srivastava, *Chem. Rec.* **2019**, *19*, 883–907.
- 11 [204] Y. Xian, Y. Xian, L. Zhou, F. Wu, Y. Ling, L. Jin, *Electrochem. Commun.* **2007**, *9*,
12 142–148.
- 13 [205] F. Arduini, L. Micheli, D. Moscone, D. Palleschi, S. Piermarini, F. Ricci, G. Volpe,
14 *Trends Anal. Chem.* **2016**, *79*, 114–126.
- 15 [206] X. Huang, D. Xu, J. Chen, J. Liu, Y. Li, J. Song, X. Ma, J. Guo, *Analyst* **2018**, *143*,
16 5339–5351.
- 17 [207] A. Walcarius, M. M. Collinson, *Annu. Rev. Anal. Chem.* **2009**, *2*, 121–143.
- 18 [208] M. Hasanzadeh, N. Shadjou, M. Eskandani, M. de la Guardia, *Trends Anal. Chem.*
19 **2012**, *40*, 106–118.

- 1 [209] H. Kholafazad Kordasht, M. Pazhuhi, P. Pashazadeh-Panahi, M. Hasanzadeh, N.
2 Shadjou, *Trends Anal. Chem.* **2020**, *124*, 115778.
- 3 [210] Z. Wang, M. Etienne, G.-W. Kohring, Y. Bon Saint Côme, A. Kuhn, A. Walcarius,
4 *Electrochim. Acta* **2011**, *56*, 9032-9040.
- 5 [211] Z. Wang, M. Etienne, S. Pöller, W. Schuhmann, G.-W. Kohring, V. Mamane, A.
6 Walcarius, *Electroanalysis* **2012**, *24*, 376–385.
- 7 [212] T. Rozhanchuk, O. Tananaiko, I. Mazurenko, M. Etienne, A. Walcarius, V. Zaitsev,
8 *J. Electroanal. Chem.* **2009**, *625*, 33–39.
- 9 [213] A. A. Kornii, A. S. Borets, O. Yu. Tananaiko, *Methods Objects Chem. Anal.* **2021**,
10 *16*, 61–70.
- 11 [214] A. Kornii, V. Saska, V. V. Lisnyak, O. Tananaiko, *Electroanalysis*, **2020**, *32*, 1468–
12 1479.
- 13 [215] O. Lev, D. Rizkov, S. Mizrahi, I. Ekeltchik, Z. G. Kipervaser, V. Gitis, A. Goifman,
14 D. Tessema, A. Kamyshny Jr., A. D. Modestov, J. Gun, in: L. Klein, M. Aparicio, A.
15 Jitianu (eds.), *Handbook of Sol-Gel Science and Technology*, Springer, Cham, 2018, pp.
16 2663–2694.
- 17 [216] B. Chen, H. Wang, H. Zhang, Z. He, S. Zhang, T. Liu, Y. Zhou, *J. Mol. Liq.* **2012**,
18 *171*, 23–28.
- 19 [217] Z. Wang, M. Etienne, F. Quilès, G.-W. Kohring, A. Walcarius, *Biosens.*
20 *Bioelectron.* **2012**, *32*, 111–117.

- 1 [218] L. Zajun, W. Zhongyun, S. Xiulan, F. Yinjun, C. Peipei, *Talanta* **2010**, *80*, 1632–
2 1637.
- 3 [219] W.-L. Zhu, Y. Zhou, J.-R. Zhang, *Talanta* **2009**, *80*, 224–230.
- 4 [220] P. N. Bartlett, F. A. Al-Lolage, *J. Electroanal. Chem.* **2018**, *819*, 26–37.
- 5 [221] I. Mazurenko, O. Tananaiko, O. Biloivan, M. Zhybak, I. Pelyak, V. Zaitsev, M.
6 Etienne, A. Walcarius, *Electroanalysis* **2015**, *27*, 1685–1692.
- 7 [222] J. Liu, D. He, Q. Liu, X. He, K. Wang, X. Yang, J. Shangguan, J. Tang, Y. Mao,
8 *Anal. Chem.* **2016**, *88*, 11707–11713.
- 9 [223]. Wang, M. Etienne, V. Urbanova, G.-W. Kohring, A. Walcarius, *Anal. Bioanal.*
10 *Chem.* **2013**, *405*, 3899–3906.
- 11 [224] S. Manivannan, K. Kim, *Electroanalysis* **2016**, *28*, 1608–1616.
- 12 [225] N. Allali, V. Urbanova, M. Etienne, X. Devaux, M. Mallet, B. Vigolo, J.-J. Adjizian,
13 C. P. Ewels, S. Oberg, A. V. Soldatov, E. McRae, Y. Fort, M. Dossot, V. Mamane,
14 *Beilstein J. Nanotechnol.* **2018**, *9*, 2750–2762.
- 15 [226] Yu. V. Iminova, O. Yu. Tananaiko, T. S. Rozhanchuk, T. G. Gruzina, L. S.
16 Reznichenko, L. Malysheva, Z. R. Ulberg. *J. Anal. Chem. (Russia)* **2015**, *70*, 1247–1253.
- 17 [227] S. Sladkevich, J. Gun, P. Prikhodchenko, D. Rizkov, R. Shelkov, N. Kyi, V. Gutkin,
18 O. Lev, Selected Contemporary Topics in Sol-Gel Electro-Chemistry. In: Sol-Gel
19 Methods for Materials Processing. NATO Science for Peace and Security Series C:
20 Environmental Security. Eds: Innocenzi P., Zub Y.L., Kessler V.G.– 2008 Springer:
21 Dordrecht. pp. 155-186.

- 1 [228] F. Wu, T. Huang, Y. Hu, X. Yang, Q. Xie, *J. Electroanal. Chem.* **2016**, *781*, 296–
2 303.
- 3 [229] B. Wang, J.-J. Zhang, Z.-Y. Pan, X.-Q. Tao, H.-S. Wang, *Biosens. Bioelectron.*
4 **2009**, *24*, 1141–1145.
- 5 [230] A. Walcarius, *Trends Anal. Chem.* **2012**, *38*, 79–97.
- 6 [231] M. M. Richter, *Chem. Rev.* **2004**, *104*, 3003–3036.
- 7 [232] C. Ma, Y. Cao, X. Gou, J.-J. Zhu, *Anal. Chem.* **2020**, *92*, 431–454.
- 8 [233] X. Ma, W. Gao, F. Du, F. Yuan, J. Yu, Y. Guan, N. Sojic, G. Xu, *Acc. Chem. Res.*
9 **2021**, *54*, 2936–2945.
- 10 [234] H. Wei, E. Wang, *Trends Anal. Chem.* **2008**, *27*, 447–459.
- 11 [235] L. Qian, X. Yang, *Anal. Chim. Acta* **2008**, *609*, 210–214.
- 12 [236] L. Armelao, R. Bertinello, S. Gross, D. Badocco, P. Pastore, *Electroanalysis* **2003**,
13 *15*, 803–811.
- 14 [237] J.-K. Lee, S.-H. Lee, M. Kim, H. Kim, D.-H. Kim, W.-Y. Lee, *Chem. Commun.*
15 **2003**, 1602–1603.
- 16 [238] H. Wang, G. Xu, S. Dong, *Analyst* **2001**, *126*, 1095–1099.
- 17 [239] C. Yi, Y. Tao, B. Wang, X. Chen, *Anal. Chim. Acta* **2005**, *541*, 73–81.
- 18 [240] B. Qiu, X. Chen, H.-L. Chen, G.-N. Chen, *Luminescence* **2007**, *22*, 189–194.
- 19 [241] L. Yang, L. Li, Y. Luo, R.-R. Zhang, Y. Cui, F. H. Cui, K. Sun, Y.-O. Li, *Chin. J.*
20 *Anal. Chem.* **2015**, *43*, 547–552.

- 1 [242] J. Wei, L. Chen, X. Cai, W. Lai, X. Chen, Z. Cai, *Biosens. Bioelectron.* **2022**, *216*,
2 114664.
- 3 [243] R. Lei, X. Wang, S. Zhu, N. Li, *Sens. Actuat. B* **2011**, *158*, 124–129.
- 4 [244] Z. Xu, Z. Guo, S. Dong, *Biosens. Bioelectron.* **2005**, *21*, 455–461.
- 5 [245] L. Zhang, Z. Xu, S. Dong, *Anal. Chim. Acta* **2006**, *575*, 52–56.
- 6 [246] L. Deng, L. Zhang, L. Shang, S. Guo, D. Wen, F. Wang, S. Dong, *Biosens.*
7 *Bioelectron.* **2009**, *24*, 2273–2276.
- 8 [247] A. Sassolas, L. J. Blum, B. D. Leca-Bouvier, *Sens. Actuat. B* **2009**, *139*, 214–221.
- 9 [248] B. D. Leca-Bouvier, A. Sassolas, L. J. Blum, *Anal. Bioanal. Chem.* **2014**, *406*,
10 5657–5667.
- 11 [249] J. Zhou, X. Lv, J. Jia, Z. Din, S. Cai, J. He, F. Xie, J. Cai, *Biosensors* **2022**, *12*,
12 1046.
- 13 [250] H. Nasrollahpour, M. Mahdipour, I. Isildak, M.-R. Rashidi, A. Naseri, B.
14 Khalilzadeh, *Biosens. Bioelectron.* **2021**, *178*, 113023.
- 15 [251] Y. Li, Z. Ding, Y. Bao, K. Han, G. Li, *Anal. Lett.* **2022**, *55*, 203–214.
- 16 [252] T. Zhang, Y. Chai, R. Yuan, J. Guo, *Mater. Sci. Eng. C* **2012**, *32*, 1179–1183.
- 17 [253] A. Ruiz-Gonzalez, J. Huang, C. Xun, R. Chhabra, R. Lee, H. Yizhong, A.
18 Davenport, B. Li, R. Palgrave, K. L. Choy, *Appl. Mater. Today* **2022**, *29*, 101600.
- 19 [254] T. Ahuja, D. Kumar, N. Singh, A. M. Biradar, Rajesh, *Mater. Sci. Eng. C* **2011**, *31*,
20 90–94.

- 1 [255] J.-H. Zhou, L.-L. Jiang, L.-K. Wu, J.-M. Hu, *Electrochem. Comm.* **2015**, *61*, 40–44.
- 2 [256] S. Guo, Z. Wang, Z. Xu, S. Wang, K. Wu, S. Chen, Z. Zhang, C. Xu, W. Qiu, L. Li,
3 *Chin. Chem. Lett.* **2017**, *28*, 2143–2146.
- 4 [257] Y. Bai, X. Liu, L. Chen, K.-u. Haq, M. A. Khan, W. Q. Zhu, X. Y. Jiang Z. L.
5 Zhang. *Microelectron. J.* **2007**, *38*, 1185–1190.
- 6 [258] M. D. Morales-Acosta, M. A. Quevedo-López, R. Ramírez-Bon, *Mater. Chem.*
7 *Phys.* **2014**, *146*, 380–388.
- 8 [259] J. Hu, W. Que, H. Liu. *Mater. Lett.* **2020**, *317*, 132120.
- 9 [260] M. B. Ali, A. Abdelghani, H. B. Ouada, N. Jaffrezic-Renault, R. Lamartine, *Mater.*
10 *Sci. Eng. C* **2002**, *21*, 29–34.
- 11 [261] F. Abdelmalek, M. Shadaram, H. Boushriha, *Sens. Actuat. B* **2001**, *72*, 208–213.
- 12 [262] T. Mori, Y. Kikuzawa, K. Noda, *Jpn. J. Appl. Phys.* **2013**, *52*, 05DC02.
- 13 [263] C. Lo, S.-W. Tan, C.-Y. Wei, J.-H. Tsai, W.-S. Lour, *Int. J. Hydrogen Energy* **2013**,
14 *38*, 313–318.
- 15 [264] Y. Tang, Z. Li, X. Zu, J. Ma, L. Wang, J. Yang, B. Du, Q. Yu, *J. Hazard. Mater.*
16 **2015**, *298*, 154–161.
- 17 [265] F. Yang, J. Zhu, X. Zou, X. Pang, R. Yang, S. Chen, Y. Fang, T. Shao, X. Luo, L.
18 Zhang, *Ceram. Int.* **2018**, *44*, 1078–1085.
- 19 [266] S. Szunerits, R. Boukherroub, *Electrochem. Commun.* **2006**, *8*, 439–444.

- 1 [267] Y.-F. Huang, C.-Y. Li, I. Broadwell, J.-F. Li, D.-Y. Wu, B. Ren, Z.-Q. Tian,
2 *Electrochim. Acta* **2011**, *56*, 10652–10657.
- 3 [268] M. Chauhan, V. K. Singh, *Opt. Fiber Technol.* **2021**, *64*, 102580.
- 4 [269] S. Singh, S. K. Mishra, B. D. Gupta, *Sens. Actuat. A* **2013**, *193*, 136–140.
- 5 [270] J. Breczko, E. Regulska, A. Basa, M. Baran, K. Winkler, M. E. Plonska-Brzezinska,
6 *ECS J. Solid State Sci. Technol.* **2016**, *5*, M3018–M3025.
- 7 [271] J. D. Bass, D. Grosso, C. Boissière, E. Belamie, T. Coradin, C. Sanchez, *Chem. Mater.*
8 **2007**, *19*, 4349–4356.
- 9 [272] S. Alberti, P. Y. Steinberg, G. Giménez, H. Amenitsch, G. Ybarra, O. Azzaroni, P.
10 C. Angelomé, G. J. A. A. Soler-Illia, *Langmuir* **2019**, *35*, 6279–6287.
- 11 [273] L. Zhou, C. Cheng, X. Li, J. Ding, Q. Liu, B. Su, *Anal. Chem.* **2020**, *92*, 3844–3851.
- 12 [274] T. Fontecave, C. Sanchez, T. Azaïs, C. Boissière, *Chem. Mater.* **2012**, *24*, 4326–
13 4336.
- 14 [275] M. Etienne, S. Goubert-Renaudin, Y. Rousselin, C. Marichal, F. Denat, B. Lebeau,
15 A. Walcarius, *Langmuir* **2009**, *25*, 3137–3145.
- 16 [276] M. Tiemann, C. Weinberger, *Adv. Mater. Interfaces* **2021**, *8*, 2001153.
- 17 [277] A. Ambrosi, M. Pumera, *Chem. Soc. Rev.* **2016**, *45*, 2740–2755.
- 18 [278] R. M. Cardoso, C. Kalinke, R. G. Rocha, P. L. dos Santos, D. P. Rocha, P. R.
19 Oliveira, B. C. Janegitz, J. A. Bonacin, E. M. Richter, R. A. A. Munoz, *Anal. Chim. Acta*
20 **2020**, *1118*, 73–91.

- 1 [279] A. Abdalla, B. A. Patel, *Curr. Opin. Electrochem.* **2020**, *20*, 78–81.
- 2 [280] M. H. Omar, K. A. Razak, M. N. Ab Wahab, H. H. Hamzah, *RSC Adv.* **2021**, *11*,
- 3 16557–16571.
- 4 [281] E. S. Farrell, Y. Schilt, M. Y. Moshkovitz, Y. Levi-Kalisman, U. Raviv, S.
- 5 Magdassi, *Nano Lett.* **2020**, *20*, 6598–6605.
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Table 1. Electrochemical sensors based on composite electrodes elaborated from continuous non-ordered silica thin films modified with organic polymers, analytical reagents, and/or nanomaterials.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Ag ⁺ in water	Spin-coating	GCE/SH-SiO ₂ /PbNP	Acc. – Det.	SWV	9.3×10 ⁻¹² – 1.85×10 ⁻⁹ M	1.2×10 ⁻¹² M	10 me. (RSD = 3.1%)		88
Ascorbic acid (in human plasma)	PLD	CE/MnTTP/SiO ₂	EC	SWV	0.082 – 33 mM	0.04 mM			72
Bromate Methionine	EAD	GCE/APTES/AuNP-Rh ₂ PMo ₁₁	EC	FIA	5×10 ⁻⁶ – 10×10 ⁻⁵ M 5×10 ⁻⁶ – 50×10 ⁻⁶ M	4.0×10 ⁻⁸ M 2.5×10 ⁻⁷ M	100 inject.	1 day	79
Cd ²⁺ Cu ²⁺ Pb ²⁺ (in natural water)	SAM and spin-coating	GCE/SH-SAMMS-Nafion	Acc. – Det.	SWV	2.5–100 ppb 0–1.5 ppb	2.5 ppb 2.5 ppb 0.5 ppb	8 me. (95%)	4 days, 120 me (91%)	71
Codeine Morphine	Drop-casting	GCE/DiMeDiMOS-TMOS-PSS-Ru(bpy) ₃ ²⁺	Direct det.	ECL	2×10 ⁻⁸ – 5×10 ⁻⁵ M 1×10 ⁻⁷ – 3×10 ⁻³ M	5×10 ⁻⁹ M 3×10 ⁻⁸ M	10 me. (RSD = 4.8 & 4.2%)	5 days, 250 me (96.8%)	240
Codeine phosphate	Dip-coating	Au/SiO ₂ -NanoTiO ₂ -ZnO-CA-Ru(bpy) ₃ ²⁺	Direct det.	ECL	1.0×10 ⁻⁷ – 1.0×10 ⁻⁴ M	2.5×10 ⁻⁸ M	10 me. (92.6%)		241
Cyanide	Soaking	GE/SiO ₂ /AgNP	Acc. – Det.	CV	1.5×10 ⁻⁶ – 2.1×10 ⁻⁴ M	1.4×10 ⁻⁸ M	7 me. (RSD = 1.7%)	60 days (96.7%)	87
DNP (in environment)	Spin-coating	GCE/V ₂ O ₅ -CeO ₂ -SBA-15-poly(vitamin B1)	Acc. – Det.	CV	(3.0–30)×10 ⁻⁶ M	0.5×10 ⁻⁶ M	10 me. (97%)	30 days (95%)	81
Dopamine Acetaminophen	EAD	nanoSPCE/Fe ₂ O ₃ /nanoC/(NH ₂ -SiO ₂ +CTAB)	Acc. – Det. & EC	DPV	2×10 ⁻⁶ – 1.0×10 ⁻⁵ M 2×10 ⁻⁶ – 1.0×10 ⁻⁵ M	6×10 ⁻⁷ M 4×10 ⁻⁷ M	20 me. (~90%)	1 month (80%)	73
Dopamine Uric acid (in urine)	Drop-casting	rGO–AuNP–CS–APTES	EC	DPV	1.0×10 ⁻⁶ – 2.0×10 ⁻⁴ M 1.0×10 ⁻⁶ – 3.0×10 ⁻⁴ M	0.3×10 ⁻⁶ M 0.7×10 ⁻⁶ M	5 me. (RSD = 3.9%)	1 month (92%)	86
Dopamine Acetaminophen Uric acid (in urine)	Drop-casting	GCE/MWCNT/SiO ₂ /Nafion	EC	DPV	5.0×10 ⁻⁷ – 6.0×10 ⁻⁶ M 5.0×10 ⁻⁷ – 5.0×10 ⁻⁶ M 5.0×10 ⁻⁷ – 1.0×10 ⁻⁵ M	0.014×10 ⁻⁶ M 0.098×10 ⁻⁶ M 0.068×10 ⁻⁶ M	10 me. (RSD = 5%)		78

Table 1. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Humidity (RH)	Dropping	AuSPE/MPTMS-SiO ₂ /AuNP/GO	Direct det.	EIS	22 - 90%				76
Humidity (RH)	Dip-coating	Ag-Pd/TiO ₂ -SiO ₂ /Ce	Direct det.	EIS	15 - 90%				91
H ₂ O, NH ₃ , NO ₂	Dip-coating	Pt/SWCNT/SiO ₂	Direct det.	Res.	200 ppm				89
H ₂ O ₂	Drop-casting	GCE/SiO ₂ -AuNP	EC	A	2.5×10 ⁻⁶ - 45.0×10 ⁻⁶ M	3.15×10 ⁻⁹ M			85
Methamphetamine	Drop-casting	GCE/DiMeDiMOS-TMOS-PSS-Ru(bpy) ₃ ²⁺	Direct det.	ECL	5.0×10 ⁻⁷ - 1.0×10 ⁻⁵ M	2.0×10 ⁻⁷ M	6 me. (RSD = 1.1%)	10 days, (95%)	239
Mo ^(VI) (in vitamins)	Drop-casting	PGE/(SiO ₂ +PDMDA)/LG	Acc. - Det.	CV	2.0×10 ⁻⁶ - 10.0×10 ⁻⁵ M	1.0×10 ⁻⁶ M	5 me. (RSD = 3-5 %)	1 month (80%)	75
Nitrite	Drop-casting	GCE/SH-SiO ₂ /AgNP	EC	A	4×10 ⁻⁶ - 48×10 ⁻⁶ M	4×10 ⁻⁶ M			80
Nitrite (in water)	EAD	Au/MPTMS-TEOS-AEPTMS/K ₄ Fe(CN) ₆	EC	FIA	1.0 - 40.0 μmol L ⁻¹	0.53 μmol L ⁻¹			82
Oxalic acid	Dip-coating	FTO/Ru(bpy) ₃ Cl ₂ -SiO ₂	Direct det.	ECL-FIA	2×10 ⁻⁶ - 3×10 ⁻⁴ M	1×10 ⁻⁶ M			236
Pb ²⁺ (in urine and drinking water)	EAD	PGE/rGO/PWA/SiO ₂	Acc. - Det.	DPASV	5.0×10 ⁻¹⁰ - 5.0×10 ⁻⁷ M	2.2×10 ⁻¹¹ M	5 me. (RSD = 8.2%)	15 days	90
Tri- <i>n</i> -propylamine	Drop-casting	GCE/Ru(bpy) ₃ Cl ₂ -SiO ₂	Direct det.	ECL	5.8×10 ⁻⁸ - 2.4×10 ⁻⁴ M	5.0×10 ⁻⁹ M	8 me. (RSD = 2.6%)	35 days (92%)	235
Tri- <i>n</i> -propylamine	Spin-coating	ITO/Tetrasil-Ru(bpy') ₃ Cl ₂	Direct det.	ECL	1×10 ⁻⁶ - 1×10 ⁻³ M	1.0×10 ⁻⁶ M	8 hours (~90%)	6 months (90%)	237
Tri- <i>n</i> -propylamine Oxalate NADH	Drop-casting	GCE/(SiO ₂ -Triton X-100)+(PSS-Ru(bpy) ₃ ²⁺)	Direct det.	ECL-FIA	1×10 ⁻³ - 1 M 1×10 ⁻³ - 1 M 1×10 ⁻³ - 1 M	1×10 ⁻⁴ M 1×10 ⁻⁴ M 5×10 ⁻⁴ M	5 me. (RSD 0.9 to 3.9 %)	1 week (98%)	238

Table 1. Continued.

^a Abbreviation: DNP, 2,4-dinitrophenol; RH, relative humidity.

^b Abbreviations for silica film preparation procedures: PLD, laser ablation deposition technique; EAD, electro-assisted deposition; SAM, self-assembled monolayer.

^c Abbreviations: GCE, glassy carbon electrode; SH-SiO₂, thiol-functionalized silica; PbNP, lead nanoparticles; CE, carbon electrode; MnTTP 5,10,15,20-tetra(4-tolyl)porphyrinato manganese(III) chloride; APTES, 3-aminopropyltriethoxysilane; AuNP, gold nanoparticles; Rh₂PMo₁₁, dirhodium(II) phosphomolybdate; SH-SAMMS, thiol self-assembled monolayers on mesoporous silica; DiMeDiMOS, dimethyldimethoxysilane; TMOS, tetramethoxysilane; PSS, poly(*p*-styrene sulfonate); CA, conductive adhesive; AgNP, silver nanoparticles; SBA, Santa Barbara Amorphous; nanoSPCE, carbon nanostructured screen-printed electrodes; nanoC, carbon nanoparticles with carboxyl and fluorine containing groups; NH₂-SiO₂, amine-functionalized silica; CTAB, cetyltrimethylammonium bromide; rGO, reduced graphene oxide; AuNP, gold nanoparticles; CS, chitosan; MWCNT, multiwall carbon nanotubes; Ag-Pd/TiO₂-SiO₂/Ce, silver-palladium planar electrodes modified with TiO₂-SiO₂ composite film doped with diammonium hexanitrocerate; AuSPE, gold screen-printed electrode; MPTMS, 3-mercaptopropyltrimethoxysilane; GO, graphene oxide; SWCNT, single wall carbon nanotubes; PGE, pyrolytic graphite electrode; PDMDA, polydimethyldiallylammonium; LG, lumogallion; MPTMS, 3-mercaptopropyltrimethoxysilane; TEOS, tetraethoxysilane; AEPTMS, 3-[2-(2-aminoethylamino)ethylamino]propyltrimethoxysilane; FTO, fluorine-doped tin oxide; PWA, phosphotungstic acid; Tetrasil-Ru(bpy')₃Cl₂, tetrasilylated ruthenium trisbipyridyl chloride complex.

^d Abbreviations: Acc., accumulation; Det., detection; EC, electrocatalytic detection.

^e Abbreviations: SWV, square wave voltammetry; FIA, flow injection analysis; ECL, electrochemiluminescence; CV, cyclic voltammetry; DPV, differential pulse voltammetry; EIS, electrochemical impedance spectroscopy; Res., resistance measurement; A, amperometry; DPASW, differential pulse anodic stripping voltammetry.

^f Expressed as % of remaining response (in parentheses) after a number of measurements (me.) or injections (inject.) or as RSD (relative standard deviation) for operational stability, or the given period of storage.

Table 2. Electrochemical sensors based on composite electrodes elaborated from molecularly imprinted silica-based thin films.

Analyte ^a	Film type ^b	Electrode configuration ^c (+ MIS composition)	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Adenine Guanine	Drop casting	GCE/MIS(TEOS,polyelectrolytes(PSS+PVS or PDDA))	Acc. – Det.	CV	2.0×10 ⁻⁵ – 5.0×10 ⁻⁴ M 2.0×10 ⁻⁵ – 4.0×10 ⁻⁴ M	1.5×10 ⁻⁵ M	3 me. (RSD = 4%)	2 month (90%)	99
Benzylpenicillin (in blood plasma)	EAD	CE/Fe ₃ O ₄ @SiO ₂ -MWCNT-CS/MIS(TEOS,PTMOS,MTMOS)	Acc. – Det.	DPV	5.0×10 ⁻⁸ – 1.0×10 ⁻³ M	1.5×10 ⁻⁹ M	60 me. (96,2%)	30 days	104
Bisphenol A (in honey, tap water, grape juice)	EAD	Au/MWCNT-AuNPs/MIS(TEOS,APTES)	Acc. – Det.	A	1.13×10 ⁻⁷ – 8.2×10 ⁻³ M	3.6×10 ⁻⁹ M	5 me. (RSD = 4.8%)		105
Caffeine (in coffee and energy drink)	Spin-coating	GCE/MWCNT-VTMOS/MIS(TEOS,MTMOS,APTES)	Acc. – Det.	DPV	0.75 – 40 μM	0.22 μM	50 me. (RSD = 2.7%)	1 month	103
Chlorogenic acid (in food)	Spin-coating	Au/MPTMS/MIS(TEOS,PTEOS,APTES)	Acc. – Det.	DPV	0.5×10 ⁻⁶ – 1.4×10 ⁻⁵ M	1.5×10 ⁻⁷ M	50 me. (RSD = 2.3%)	3 month	102
Dopamine	Spin-coating	GCE/MIS(TMOS,PTMOS,MTMOS)	Acc. – Det.	CV	0 – 0.5mM		48 hr	7 days	97
Dopamine Tyramine	Spin-coating	GCE/MIS(TEOS,PTEOS)	Acc. – Det.	SWV	1.0×10 ⁻⁵ – 1.0×10 ⁻⁴ M	1.0×10 ⁻⁵ M	3 me. (RSD = 7.4%)	2 weeks (78%)	98
L-Histidine (in human blood serum)	LbL-EAD	ITO/APTES/MWCNT/MIS(TEOS,PTMOS,MTMOS)	Acc. – Det.	DPV	2.0×10 ⁻⁶ – 1.0×10 ⁻³ M	5.8×10 ⁻⁹ M	9 me. (RSD = 3.4%)		101
Methyl parathion	EAD	GCE/MIS(TEOS,VTES)	Acc. – Det.	SWV	1.0×10 ⁻⁸ – 1.0×10 ⁻⁵ M	9.0×10 ⁻⁹ M	50 me. (RSD < 5%)		109
Naloxone (in urine)	EAD	ITO/MWCNT/PPy@MIS(TEOS,PTEOS)	Acc. – Det.	DPV	0.0 – 12 μM	0.02 μM	4 sensors (RSD = 9.3%)	14 days (92%)	74
Ochratoxin A (in wheat flour)	Drop casting	MIS/PNCs-NGQDs/2D mSiO ₂ -G	Direct det.	ECL	10 ⁻⁵ – 1.0 ng/mL	0.2 pg/mL	15 me (RSD = 1.63%)		242

Table 2. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c (+ MIS composition)	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
<i>p</i> -Nitrophenol	EAD	GCE/CS/PTMOS/AuNPs	Acc. – Det.	DPV	$3.0 \times 10^{-8} - 3.5 \times 10^{-4}$ M	5.0×10^{-9} M	10 me. (RSD = 2-3%)	10 days (96%)	114
Paracetamol (in tablets and urine)	Drop-casting	GCE/GO/MIS(TEOS,PTEOS)	Acc. – Det.	DPV	$0.1 \times 10^{-6} - 8.0 \times 10^{-5}$ M	2.0×10^{-8} M	5 me. (RSD = 8.2%)	1 week (93%)	100
L-Phenylalanine (in blood plasma)	LbL-EAD	CE/PANI/ β -CD–MWCNT/MIS(TEOS,PTMOS,MTMOS)	Acc. – Det.	DPV	$1 \times 10^{-7} - 1.0 \times 10^{-4}$ M	1.0×10^{-9} M	5 sensors (RSD = 4.1%)	1 month (92,3%)	106
Tetracycline (in water & serum)	Drop-casting	GCE/L-His–MWCNT@PDMS-5/MIS(TEOS,CTAB)	Acc – Det.	DPV	$1 \times 10^{-11} - 1 \times 10^{-10}$ M	2.64×10^{-12} M (in water) & 2.20×10^{-12} M (in serum)			113
Thymidine (in tablets)	LbL-EAD	CE/MWCNT/MIS(TEOS,VTMOS,MTMOS)	Acc. – Det.	DPV	$2.0 \times 10^{-6} - 2.2 \times 10^{-5}$ M	1.6×10^{-9} M	8 me. (RSD = 2.7%)		107

^a In parentheses are real media used for recovery measurements performed after spiking (but, unless stated otherwise, the analytical performance is given for the analysis of aqueous solutions).

^b Abbreviations for silica film preparation procedures: EAD, electro-assisted deposition; LbL, layer-by-layer.

^c Abbreviations: MIS, molecularly imprinted silica (in parenthesis, the acronyms of sol-gel precursors used for their synthesis); GCE, glassy carbon electrode; TEOS, tetraethoxysilane; PSS, poly(styrene sulfonate); PVS, poly(vinyl sulfonate); PDDA, poly(diallyldimethyl ammonium); CE, carbon electrode; Fe₃O₄@SiO₂, core-shell Fe₃O₄-SiO₂ nanoparticles; MWCNT, multiwall carbon nanotubes; CS, chitosan; PTMOS, phenyltrimethoxysilane; MTMOS, methyltrimethoxysilane; AuNPs, gold nanoparticles; APTES, 3-aminopropyltriethoxysilane; VTMS, vinyltrimethoxysilane; MPTMS, 3-mercaptopropyltrimethoxysilane; PTEOS, phenyltriethoxysilane; TMOS, tetramethoxysilane; ITO, indium-tin oxide; VTES, vinyltriethoxysilane; PPy, polypyrrole; PNCs, perovskite nanocrystals; NGQDs, N-doped graphene quantum dots; 2D mSiO₂-G, graphene supported two-dimensional mesoporous SiO₂ nanosheets; GO, graphene oxide; PANI, polyaniline; β -CD, β -cyclodextrin; L-His, L-Histidine; PDMS, poly(dimethyl siloxane); CTAB, cetyltrimethylammonium bromide.

^d Abbreviations: Acc., accumulation; Det., detection.

^e Abbreviations: CV, cyclic voltammetry; DPV, differential pulse voltammetry; A, amperometry; SWV, square wave voltammetry; ECL, electrochemiluminescence.

^f Expressed as % of remaining response (in parentheses) after a number of measurements (me.) or as RSD (relative standard deviation) for operational stability, or the given period of storage.

Table 3. Electrochemical sensors based on composite electrodes elaborated from continuous ordered mesoporous silica thin films.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Acetaminophen	EISA	AuF/CDG/OMSF	Direct det.	DPV	$2 \times 10^{-7} - 5.0 \times 10^{-5}$ M	1.4×10^{-8} M	10 me. (80%)		115
Acetaminophen Norepinephrine Tryptophan	EASA	GCE/rGO/VMSF	Acc. – Det.	DPV	$2 \times 10^{-7} - 1.0 \times 10^{-4}$ M $1 \times 10^{-7} - 3.0 \times 10^{-5}$ M $8 \times 10^{-7} - 2.0 \times 10^{-4}$ M	9.7×10^{-9} M 1.4×10^{-8} M 3.6×10^{-8} M	10 days (98.4%)		121
Ag ⁺	EISA	GCE/(OMSF-SH)	Acc. – Det.	ASDPV	$2 \times 10^{-7} - 1.0 \times 10^{-5}$ M	6×10^{-9} M			116
Ascorbic acid	Stöber	ITO/(VMSF-PANI)	EC	CV	$1 \times 10^{-4} - 1.0 \times 10^{-2}$ M	-			158
Ascorbic acid	Stöber	ITO/(VMSF-NH ₂ /AuNPs)	EC	DPV	$5 \times 10^{-5} - 1.0 \times 10^{-2}$ M	-			159
Ascorbic acid Cu ²⁺	EASA	Au/(VMSF-GPS-DNAzyme)	Indirect det.	SWV	$1.0 \times 10^{-6} - 1.2 \times 10^{-4}$ M 310 ppb – 4.5 ppm	7.0×10^{-7} M 250 ppb			122
Bisphenol A	Stöber	ITO/(VMSF-PDMS)	Acc. – Det.	DPV	$1.0 \times 10^{-6} - 2.0 \times 10^{-5}$ M & 2.0×10^{-5} M – 1.0×10^{-4} M	2.3×10^{-7} M	10 h - 6 me. (~90%)	5 days (100%)	160
<i>tert</i> - butylhydroquinone	EASA	GCE/ErGO/VMSF	Acc. – Det.	DPV	$1 \times 10^{-9} - 5 \times 10^{-7}$ M & $5 \times 10^{-7} - 1.2 \times 10^{-4}$ M	2.3×10^{-10} M	20 min (real media)		123
Carbendazim	EASA	GCE/BN-rGO/VMSF	Acc. – Det.	DPV	$5 \times 10^{-9} - 7 \times 10^{-6}$ M	2.3×10^{-9} M			124
Cardiac Troponin I	Stöber	ITO/(VMSF-NH ₂ -Tro4 Apt)	Aptasensing	EIS ECL	$0.05 \text{ pg mL}^{-1} - 1 \text{ ng mL}^{-1}$ $0.05 \text{ pg mL}^{-1} - 10 \text{ ng mL}^{-1}$	0.05 pg mL^{-1} 0.02 pg mL^{-1}	7 days (89.4%) 7 days (90.3%)		161
Catechol	Stöber	Patterned ITO/(VMSF-Ru(bpy) ₃ ²⁺ , DBAE)	Direct det.	ECL	$1.0 \times 10^{-5} - 1.0 \times 10^{-3}$ M	9.52×10^{-6} M			162
Catechol Hydroquinone	EASA	AuE/ErGO/(VMSF-CTAB) AuE/ErGO/VMSF	Acc. – Det.	DPV	$1 \times 10^{-6} - 2.0 \times 10^{-5}$ M & $2.0 \times 10^{-5} - 6.0 \times 10^{-5}$ M $1 \times 10^{-6} - 6.0 \times 10^{-5}$ M	1.7×10^{-8} M 1.5×10^{-8} M	12 min (90%)		125
CA15-3	EASA	ITO/(VMSF-GPS-Ab, Ru(bpy) ₃ ²⁺)	Immunosensing	ECL DPV	$0.0001 - 100 \text{ U mL}^{-1}$ $0.01 - 100 \text{ U mL}^{-1}$	$9 \text{ } \mu\text{U mL}^{-1}$ 5.4 mU mL^{-1}	15 days (95%)		126

Table 3. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
CEA CA15-3	EASA	ITO/(VMSF-Ru(bpy) ₃ ²⁺)/ (VMSF-NH ₂)/GluA-Ab	Immunosensing	ECL DPV	0.0001 – 50 ng mL ⁻¹ 0.005 – 500 U mL ⁻¹	0.06 pg mL ⁻¹ 2.3 mU mL ⁻¹			127
Chloramphenicol	Stöber	ITO/(VMSF-CTAB)	Acc. – Det.	DPV	0.1 – 3.7 ppm & 3.7 – 15.0 ppm	37.7 ppb			163
Chloramphenicol	Stöber	ITO/(VMSF-CTAB)	Acc. – Det.	DPV	0.3 – 5.8 ppm & 5.8 – 40 ppm (honey) 0.3 – 5.8 ppm & 5.8 – 32 ppm (milk)	148.4 ppb (honey) 80.6 ppb (milk)			164
Chlorpromazine	EASA	SPCE/ErGO/VMSF	Acc. – Det.	DPV	3×10 ⁻⁷ – 2.3×10 ⁻⁵ M & 1×10 ⁻⁶ – 1×10 ⁻⁵ M (blood)	6.1×10 ⁻⁹ M 1.6×10 ⁻⁸ M			128
Clindamycin	EASA	PET-ITO/(VMSF- Ru(bpy) ₃ ²⁺)	Direct det.	ECL	10 nM – 25 μM & 25 – 70 μM	4 nM			129
Clozapine	EASA	p-SPCE/VMSF	Acc. – Det.	DPV	50 nM – 20 μM	2.8×10 ⁻⁸ M			130
C-reactive protein	EASA	SPCE/ErGO/(VMSF- NH ₂)/GluA-Ab	Immunosensing	DPV	10 pg mL ⁻¹ – 100 ng mL ⁻¹	8 pg mL ⁻¹		7 days (91%)	131
Cu ²⁺	EASA	GCE/(clay + VMSF)	Acc. – Det.	SWV	1×10 ⁻⁷ – 1.0×10 ⁻⁶ M	-			132
Cu ²⁺	EASA	GCE/(VMSF-NH ₂)	Acc. – Det.	ASDPV	1×10 ⁻⁸ – 1.0×10 ⁻⁶ M	3×10 ⁻⁹ M			133
Cysteine	EASA	ITO/(VMSF-Fc)	Mediated EC	A, FIA	3×10 ⁻⁶ – 1.0×10 ⁻⁴ M	-			134
Diclofenac	EASA	GCE/APTES/(Amino-AT + VMSF)	Acc. – Det.	SWV	3×10 ⁻⁷ – 2.0×10 ⁻⁵ M	5.3×10 ⁻⁸ M	3 me. (95%)		135
DNA	EASA	Au/(VMSF-GPS-DNA ab)	Genosensing	CV	5×10 ⁻⁹ – 7.0×10 ⁻⁷ M	2.5×10 ⁻⁹ M		1 month (93%)	136
Dopamine	Stöber	ITO/(VMSF-Ru(bpy) ₃ ²⁺)	Direct det.	ECL	5 nM – 20 μM	3.5×10 ⁻⁹ M		7 days	165
Dopamine Ascorbic acid	EASA	GCE/(VMSF-NMe ₃ ⁺)	Acc. – Det.	DPV	2.0×10 ⁻⁵ – 2.26×10 ⁻⁴ M 4.9×10 ⁻⁵ – 2.65×10 ⁻³ M	9×10 ⁻⁶ M 1.1×10 ⁻⁵ M			137

Table 3. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Doxorubicin	EASA	GCE/ErGO/VMSF	Acc. – Det.	DPV	1×10 ⁻⁹ –2.0×10 ⁻⁵ M	7.7×10 ⁻¹⁰ M	24 min (97%)		138
F ⁻	Stöber	ITO/(VMSF-PBA)	Indirect det.	DPV	1×10 ⁻⁹ –2.3×10 ⁻² M	8.3×10 ⁻¹⁰ M	2 h	2 months	166
Glucose	Stöber	FTO/(VMSF-NiO(OH))	EC	A	1.0×10 ⁻⁵ –1.2×10 ⁻² M	4.4×10 ⁻⁷ M			167
Guanine	EASA	ITO/(VMSF-Ru(bpy) ₃ ²⁺)	EC	CV	2×10 ⁻⁷ –5.0×10 ⁻⁴ M	5.8×10 ⁻⁸ M			139
Hg ²⁺	IA-MS-clay	GCE/(PCH-SH)	Acc. – Det.	ASSWV	5×10 ⁻⁸ –1.0×10 ⁻⁶ M	2.4×10 ⁻⁸ M			117
Hg ²⁺	EISA	GCE/(OMSF-MTTZ)	Acc. – Det.	ASSWV	5×10 ⁻⁸ –1.0×10 ⁻⁶ M	2.4×10 ⁻⁸ M			118
Hg ²⁺	Stöber	ITO/(VMSF-GQDs)	Acc. – Det.	ASDPV	10 pM–1.0 nM & 1.0 nM–0.5 μM	9.8 pM			181
Cu ²⁺				ASDPV	10 pM–1.0 nM & 1.0 nM–1.5 μM	8.3 pM			
Cd ²⁺				ASDPV	20 nM–1.0 μM & 1.0 μM–20 μM	4.3 nM			
Dopamine				EASA	AuE/(VMSF-GQDs)	DPV	200 nM–20 μM & 20–100 μM	120 nM	
Hydrogen peroxide	EASA	ITO/(VMSF-PB wires)	Mediated EC	CV	1×10 ⁻⁴ –1×10 ⁻² M			140	
Hydrogen peroxide	EASA	ITO/(VMSF-Fe(Htrz) ₃)	Mediated EC	A, FIA	5×10 ⁻⁶ –3.0×10 ⁻⁴ M	2×10 ⁻⁶ M			141
Hydrogen peroxide	Stöber	ITO/(VMSF-PANI/PtNPs)	EC	A	1.0×10 ⁻⁶ –2.0×10 ⁻³ M	2.4×10 ⁻⁷ M			168
Hydrogen peroxide	Stöber	ITO/(VMSF, luminol)	Direct det.	ECL	5×10 ⁻⁶ –1×10 ⁻³ M	5×10 ⁻⁶ M			169
Hydrogen peroxide	Stöber	ITO/(VMSF-NMe ₃ ⁺ - AuNPS, luminol)	Direct det.	ECL	1×10 ⁻⁷ –2.0×10 ⁻⁴ M	2.53×10 ⁻⁸ M			170
Hydrogen peroxide	Stöber	ITO/(VMSF-PtNS)	EC	A	1×10 ⁻⁵ –5.0×10 ⁻³ M	-	50 min (100%)	182	
	EASA	CFME/(VMSF-PtNS)			5×10 ⁻⁴ –2.0×10 ⁻³ M	-	90 min (in brain)		

Table 3. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Imidacloprid	EASA	GCE/ErGO/VMSF	Acc. – Det.	CV	1.0 µg mL ⁻¹ – 50 µg mL ⁻¹ & 50 µg mL ⁻¹ – 400 µg mL ⁻¹	0.3 µg mL ⁻¹		5 days (94%)	142
Insulin	EASA	GCE/APTES/(VMSF-NH ₂)/GluA-cDNA-Apt.	Aptasensing	DPV	1.0×10 ⁻⁸ – 3.5×10 ⁻⁷ M	3.0×10 ⁻⁹ M	5 me.		143
Isoproturon	EASA	GCE/APTES/VMSF	EO amplif.	SWV	1.0×10 ⁻⁵ – 1.0×10 ⁻⁴ M	-			144
Lidocaine	EASA	FTO/(VMSF-Ru(bpy) ₃ ²⁺)	Direct det.	ECL	1.0×10 ⁻⁸ – 5.0×10 ⁻⁵ M	8×10 ⁻⁹ M			145
Matrine	Stöber	P-µchip/ITO/(VMSF-Ru(bpy) ₃ ²⁺)	Direct det.	ECL	1×10 ⁻⁷ – 5.0×10 ⁻⁵ M	4.02×10 ⁻⁹ M			171
Metoprolol					1×10 ⁻⁷ – 1.0×10 ⁻⁴ M	11.4×10 ⁻⁹ M			
Chlorphenamine					1×10 ⁻⁷ – 1.0×10 ⁻⁴ M	9.05×10 ⁻⁹ M			
Lincomycin					1×10 ⁻⁷ – 1.0×10 ⁻⁴ M	4.01×10 ⁻⁹ M			
Levosulpiride					1×10 ⁻⁷ – 2.5×10 ⁻⁵ M	3.04×10 ⁻⁹ M			
Sophoridine					1×10 ⁻⁷ – 4.0×10 ⁻⁵ M	1.80×10 ⁻⁹ M			
Sophocarpine					1×10 ⁻⁷ – 5.0×10 ⁻⁵ M	2.70×10 ⁻⁹ M			
Methidazine	EASA	3DG/VMSF	Acc. – EC Det.	DPV	5.0×10 ⁻⁸ – 1×10 ⁻⁵ M	3.0×10 ⁻⁸ M	5 me.		146
Nicotine	Stöber	ITO/(VMSF-Ru(bpy) ₃ ²⁺)	Direct det.	ECL	1×10 ⁻⁷ – 1.5×10 ⁻⁵ M	2.78×10 ⁻⁸ M			172
Nitrate	EASA	ITO/(VMSF-Fc)	Indirect det.	IC-A	2.0×10 ⁻⁵ – 1.0×10 ⁻⁴ M	1.6×10 ⁻⁵ M			147
Fluoride					5×10 ⁻⁶ – 5.0×10 ⁻⁵ M	3×10 ⁻⁶ M			
Chloride					5×10 ⁻⁶ – 5.0×10 ⁻⁵ M	4×10 ⁻⁶ M			
Bromide					1.0×10 ⁻⁵ – 7.5×10 ⁻⁵ M	1.0×10 ⁻⁵ M			
Phosphate					2.0×10 ⁻⁵ – 1.0×10 ⁻⁴ M	1.2×10 ⁻⁵ M			
Sulfate					1.5×10 ⁻⁵ – 1.0×10 ⁻⁴ M	1.0×10 ⁻⁵ M			
<i>p</i> -NCB	Stöber	ITO/(VMSF-CTAB)	Acc. – Det.	DPV	6 – 302 ppb & 302 – 1500 ppb	5.52 ppb			173
<i>m</i> -NCB					5 – 147 ppb & 147 – 1000 ppb	0.98 ppb			
<i>p</i> -NBB					8 – 136 ppb & 136 – 1000 ppb	3.55 ppb			
DNBB					6 – 259 ppb & 259 – 2000 ppb	4.23 ppb			

Table 3. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Paraoxon Methyl parathion Fenitrothion	Stöber	ITO/(VMSF-PDMS)	Acc. – Det.	DPV	5 – 1000 ppb 5 – 1000 ppb 50 – 600 & 600 – 2000 ppb	1.83 ppb 2.59 ppb 17.2 ppb			174
Paraoxon Methyl parathion Fenitrothion	Stöber	ITO/(VMSF-CTAB)	Acc. – Det.	DPV	5 – 385 ppb & 385 – 2000 ppb 5 – 136 ppb & 136 – 1000 ppb 400 – 7000 ppb	3.53 ppb 3.01 ppb 114.86 ppb			175
Paraquat	EASA	GCE/APTES/VMSF	Acc. – Det.	SWV	1.0×10^{-8} – 1.0×10^{-5} M	4×10^{-9} M			148
Paraquat	EASA	GCE/3DG-CNT/VMSF	Acc. – Det.	DPV	2×10^{-9} – 1.0×10^{-8} M & 1.0×10^{-8} – 1.0×10^{-5} M	1.17×10^{-9} M	5 days (93%)		149
Pb ²⁺	Spin-coating	Au/(OMSF-SH)	Acc. – Det.	SWV	250 – 5000 ppb & 25 – 100 ppb	250 ppb & 25 ppb			119
pH	Stöber	ITO/(VMSF-i-motif DNA)	Direct det.	DPV	pH 5 – 8	-			176
PSA	EASA	ITO/(VMSF-NH ₂)/GluA-Ab)	Immunosensing	DPV	10 pg mL ⁻¹ – 1 µg mL ⁻¹	8.1 pg mL ⁻¹	6 days (91.5%)		150
PSA	EASA	ITO/VMSF/GPS-Ab	Immunosensing	ECL	1 pg mL ⁻¹ – 100 ng mL ⁻¹	0.1 pg mL ⁻¹	15 days (97.2%)		151
PSA	EASA	Au/(VMSF-GPS-PSA Apt.)	Aptasensing	DPV	1 – 300 ng mL ⁻¹	0.28 ng mL ⁻¹	30 days (97%)		152
Retinol Trolox	Stöber	ITO/(VMSF-CTAB)	Acc. – Det.	DPV	1×10^{-6} – 6.0×10^{-5} M 1×10^{-6} – 1.0×10^{-4} M	6.5×10^{-7} M 2.9×10^{-7} M			177
Rutin	EASA	GCE/ErGO/VMSF	Acc. – Det.	DPV	3×10^{-7} – 2×10^{-6} M & 2×10^{-6} – 4.0×10^{-5} M	2.3×10^{-9} M	10 min (95%)		153

Table 3. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Serotonin	EASA	ITO/ErGO-CNT/VMSF	Direct det.	DPV	1×10 ⁻⁷ –1.0×10 ⁻⁵ M	5.4×10 ⁻⁹ M			164
Melatonin					1.0×10 ⁻⁵ –3.0×10 ⁻⁵ M 1×10 ⁻⁶ –2.0×10 ⁻⁵ M 2.0×10 ⁻⁵ –1.0×10 ⁻⁴ M	1.41×10 ⁻⁸ M			
TMB	Stöber	ITO/(VMSF-CTAB)	Direct det.	DPV	1×10 ⁻⁷ –1.0×10 ⁻⁵ M	1.7×10 ⁻⁸ M	'pretty good'		178
K ⁺	Stöber	ITO/(VMSF-CTAB) (+TMB and G4zyme in solution)	Indirect det. (TMB responsive)	DPV	10 ⁻⁶ –10 ⁻⁵ M & 10 ⁻⁵ –10 ⁻³ M	9.3×10 ⁻⁷ M			178
ATP					10 ⁻⁵ –1.5×10 ⁻³ M	9.6×10 ⁻⁶ M			
Thrombin					10 ⁻⁷ –10 ⁻⁶ M	9.8×10 ⁻⁸ M			
DNA					5×10 ⁻¹⁰ –5×10 ⁻⁸ M	3.98×10 ⁻¹⁰ M			
TNT	Stöber	ITO/(VMSF-Ru(bpy) ₃ ²⁺)	Direct det.	ECL	10 ⁻⁷ –10 ⁻³ mg/mL	2.3×10 ⁻⁹ mg/mL			179
TNT	Stöber	ITO/(VMSF-CTAB)	Acc. – Det.	DPV	10–1000 ppb	4.97 ppb			175
DNT					10–1000 ppb	5.87 ppb			
TNP					2–80 ppb	1.46 ppb			
NP					40–2000 ppb	12.90 ppb			
NB					10–3000 ppb	14.28 ppb			
2,4,6-trichlorophenol	EASA	3DG/VMSF	Acc. – EC Det.	DPV	1.0×10 ⁻⁸ –1×10 ⁻⁷ M & 1×10 ⁻⁷ –1.5×10 ⁻⁵ M	2.4×10 ⁻⁹ M	5 me.		155
Tri- <i>n</i> -propylamine	Stöber	ITO/(VMSF-Ru(bpy) ₃ ²⁺)	Direct det.	ECL	0.5 nM–15.8 μM & 15.8–150 μM	0.17 nM			180
Nicotine					0.565–75.1 μM & 75.1–500 μM	565 nM			
Atropine					0.2–82.9 μM & 82.9–500 μM	85 nM			
L-Tryptophan	EISA	ITO/(Trp-MI-OMSF-NH ₂)	Acc. – Det.	DPV	2×10 ⁻⁴ –4.0×10 ⁻³ M	1.06×10 ⁻⁴ M			120
D-Tryptophan					2×10 ⁻⁴ –4.0×10 ⁻³ M	1.27×10 ⁻⁴ M			

Table 3. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Uric acid	EASA	pl-3DG/VMSF	Direct det.	DPV	100 nM – 30 μ M & 30 – 150 μ M	2.3 \times 10 ⁻⁸ M			156
Uric acid	EASA	SPCE/ErGO/(VMSF-NH ₂)	Direct det.	DPV	5 \times 10 ⁻⁷ – 1.80 \times 10 ⁻⁴ M	1.29 \times 10 ⁻⁷ M	7 days (97.1%)		157

^a Abbreviations: CA15-3, cancer antigen 15-3; CEA, carcino-embryonic antigen; DNA, deoxyribonucleic acid; *p*-NCB, 1-chloro-4-nitrobenzene; *m*-NCB, 1-chloro-3-nitrobenzene; *p*-NBB, 1-bromo-4-nitrobenzene; DNBB, 2,4-dinitrobenzene; PSA, prostate specific antigen; TMB, 3,3',5,5'-tetramethylbenzidine; ATP, adenosine 5'-triphosphate; TNT, 2,4,6-trinitrotoluene; DNT, 2,6-dinitrotoluene; TNP, 2,4,6-trinitrophenol; NP, 3-nitrophenol; NB, nitrobenzene.

^b Abbreviations for ordered mesoporous film preparation procedures: EISA, evaporation-induced self-assembly; EASA, electrochemically assisted self-assembly; Stöber, Stöber growth method; IA-MS-clay, intragallery assembly of mesoporous organosilica in smectite clay.

^c Abbreviations: AuF, gold film; CDG, β -cyclodextrin-graphene; OMSF, ordered mesoporous silica film; VMSF, vertically-oriented mesoporous silica film; GCE, glassy carbon electrode; rGO, reduced graphene oxide; VMSF-SH, thiol-functionalized vertically-oriented mesoporous silica film; ITO, indium-tin oxide; PANI, polyaniline; VMSF-NH₂, amine-functionalized vertically-oriented mesoporous silica film; AuNPs, gold nanoparticles; GPS, (3-glycidopropyl) trimethoxysilane; DNAzyme, deoxyribozyme; PDMS, polydimethylsiloxane; ErGO, electrochemically reduced graphene oxide; BN-rGO, boron nitride-reduced graphene oxide; Tro4 Apt, aminated troponin aptamer; Ru(bpy)₃²⁺, tris(2,2'-bipyridyl)ruthenium(II); DBAE, *N,N*-dibutylethanolamine; AuE, gold electrode; CTAB, cetyltrimethylammonium bromide; Ab, antibody; GluA, glutaraldehyde; SPCE, screen-printed carbon electrode; PET-ITO, polyethyleneterephthalate coated with indium-tin oxide; p-SPCE, electrochemically pretreated screen-printed electrode; Fc, ferrocene; APTES, aminopropyl-triethoxysilane; Amino-AT, amino-attapulgit; VMSF-NMe₃⁺, trimethylammonium-functionalized vertically-oriented mesoporous silica film; PBA, phenylboronic acid; FTO, fluorine-doped tin oxide; PCH-SH, thiol-functionalized porous clay heterostructure; MTTZ, 5-mercapto-1-methyl-1H-tetrazole; PB, Prussian Blue; Fe(Htrz)₃, iron-triazole coordination polymer (Htrz=1,2,4,-1H-triazole); GQDs, graphene quantum dots; PtNPs, platinum nanoparticles; PtNS, platinum nanostructure; CFME, carbon fiber microelectrode; cDNA, complementary DNA oligonucleotide; Apt., aptamer; P- μ chip, paper microchip; 3DG, 3D graphene; 3DG-CNT, 3D graphene-carbon nanotube assemblies; PSA Apt., prostate specific antigen aptamer; TMB, 3,3',5,5'-tetramethylbenzidine; G4zyme, G-quadruplex/hemin DNAzyme; Trp-MI, molecularly imprinted tryptophan; pl-3DG, plasma-treated 3D graphene.

^d Abbreviations: Det., detection; Acc., accumulation; EC, electrocatalysis; EO amplif., electro-oligomerisation signal amplification.

^e Abbreviations: DPV, differential pulse voltammetry; ASDPV, anodic stripping differential pulse voltammetry; CV, cyclic voltammetry; EIS, electrochemical impedance spectroscopy; ECL, electrochemiluminescence; SWV, square wave voltammetry; A, amperometry; FIA, Flow injection analysis; ASSWV, anodic stripping square wave voltammetry; IC-A, ion chromatography with amperometric detection.

^f Expressed as % of remaining response (in parentheses) after a number of measurements (me.) or minutes/hours (min/h) of use (operational stability), or the given period of storage.

Table 4. Electrochemical sensors based on biocomposite electrodes elaborated from silica thin films and biomolecules.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
AFB1 (in bee pollen)	Drop-casting	GCE/SiO ₂ -IL/AFB1 AB	Immunosensor Acc. – Det.	EIS	0.1 – 10 ng mL ⁻¹	0.01 ng mL ⁻¹	6 me. (RSD = 1.6%)	180 days (95%)	218
BCR/ABL (in human serum)	EAD	GE/SiO ₂ -luminol/AuNP/Fc-MB	Genosensor Acc. – Det.	ECL	1.0×10 ⁻¹⁵ – 1.0×10 ⁻⁹ M	4.6×10 ⁻¹⁶	100 me. (RSD = 1.15%)		251
Choline (in food and blood serum)	EAD	SPCE/SiO ₂ -ChOx	EC	A	1.60 – 65.50 mg L ⁻¹	1.0 mg L ⁻¹		3 weeks (93%)	221
Choline	Drop-casting	SPCE/Polyluminol/SiO ₂ -Nafion-ChOx	EC	ECL	4×10 ⁻⁷ – 1.3×10 ⁻⁴ M				247
D-sorbitol (in food and cosmetics)	LbL-ED-EAD	SPCE/MWCNT/SiO ₂ -DSDH	EC	A	0.5×10 ⁻³ – 3.5×10 ⁻³ M	0.16×10 ⁻³ M		1 month (90%)	37
D-sorbitol	LbL-EAD	GCE/MWCNT-Os/SiO ₂ -PEI-DI-DSDH-NADGPS	EC	A	0.4 – 2.8 mM				211
D-sorbitol	LbL-EAD	GCE/(MWCNT+CS)-PMG/SiO ₂ -DSDH-NADGPS	EC	A	0.1 – 1.0 mM	0.11 mM			223
D-sorbitol D-glucose Lactic acid	Drop-casting	GCE/SiO ₂ -(DSDH+DI)-(PEI-Fc)-(NADGPS)	EC	CV, A			12 h		217
Ethanol	Drop-casting	GCE/SiO ₂ -PVA4VP-Nafion-Ru(bpy) ₃ ²⁺ -ADH	Direct det.	ECL	2.5×10 ⁻⁵ – 5.0×10 ⁻² M	1.0×10 ⁻⁵ M	15 me. (RSD < 5%)	1 week (70%)s	244
Ethanol	Drop-casting	GCE/SiO ₂ -CS-PSS-Ru(bpy) ₃ ²⁺ -ADH	Direct det.	ECL	2.79×10 ⁻⁵ – 5.78×10 ⁻² M	9.3×10 ⁻⁶ M	100 me. (RSD = 7%)	10 days	245
Ethanol	Immersion	Au/PSSG/AuNP/Ru(bpy) ₃ ²⁺ /ADH	EC	ECL	5.0×10 ⁻⁶ – 5.2×10 ⁻³ M	12×10 ⁻⁹ M	10 me. (RSD = 0.6%)	1 week (85%)	246
NADH		Au/PSSG/AuNP/Ru(bpy) ₃ ²⁺			2.5×10 ⁻⁹ – 5.9×10 ⁻⁴ M	1×10 ⁻⁹ M			

Table 4. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
Glucose	Spreading	CSPE/SiO ₂ -PVA/GOx	EC	A	0–4.13×10 ⁻³ M	9.8×10 ⁻⁶ M			77
Glucose	EAD	Au or (Pt nano/Au)/GOx-APTES-CS	EC	A	0.2×10 ⁻⁶ –8.2×10 ⁻³ M	0.2×10 ⁻⁶ M	10 me. (RSD = 2%)	6 month	51
Glucose (in juice, serum blood)	EAD	Au/SiO ₂ -Hb-GOx-AuNP	EC	CV	1.5×10 ⁻⁵ –2.0×10 ⁻⁴ M	8.0×10 ⁻⁶ M	10 me. (85%)	3 weeks (95%)	226
Glucose	Drop-casting and spreading	ITO/Ru(bpy) ₃ ²⁺ /SiO ₂ /GDH/Resydrol	Direct det.	ECL	2.5×10 ⁻⁵ –2.0×10 ⁻⁴ M	0.5×10 ⁻⁶ M			243
H ₂ O ₂	Drop-casting	GCE/HAp/SiO ₂ /HRP	EC	A	1×10 ⁻⁶ –1.0×10 ⁻⁶ M	0.35×10 ⁻⁶ M	2 h (96%)	2 weeks (95%)	229
H ₂ O ₂	LbL-drop-casting	ITO/AuNP+SiO ₂ /RGO-CD/HRP-ADA	EC	CV	0.25–1.0 mM				224
H ₂ O ₂	Casting	CPE/DTAB/PANI-SiO ₂ /Hb	EC	CV	0.09×10 ⁻³ –2.8×10 ⁻³ M	0.03×10 ⁻³ M			216
H ₂ O ₂	EAD	CE/SiO ₂ -Hb	EC	CV	0.034–0.14 mg L ⁻¹	0.017 mg L ⁻¹			40
H ₂ O ₂ Nitrite	LbL-Spreading	GCE/RTIL-sol-gel/GNRs@SiO ₂ -Mb	EC	CV	0.2×10 ⁻⁶ –1.8×10 ⁻⁴ M 0.04×10 ⁻³ –5.0×10 ⁻³ M	0.12×10 ⁻⁶ M 0.02×10 ⁻³ M		21 days (93%)	219
Lysozyme Adenosine K ⁺	Stöber and drop-casting	ITO/MSFs@Ru-Aptamer	Aptasensor Acc. – Det.	ECL	1–100 μM 1 nM–10 μM 0.1 nM–1 μM	0.06 nM 0.75 nM 0.5 μM	5 me. (RSD = 5.95%)		222
Maltose (in food)	EAD	SPCE/SiO ₂ +CuO/GOx+Malt	EC	CV	1.0×10 ⁻⁵ –1.0×10 ⁻⁴ M	5.0×10 ⁻⁶ M	15 me. (RSD = 2%)		214
O ₂ (in tap water) Rimantadine	EAD	PGE/SiO ₂ -AuNP/Hb	EC EC-Inh	CV	0.5–9.0 mg L ⁻¹ 0.5–2.0 mg L ⁻¹	0.12 mg L ⁻¹ 0.30 mg L ⁻¹	30 scans (85%)		212

Table 4. Continued.

Analyte ^a	Film type ^b	Electrode configuration ^c	Detection method		Analytical performance		Stability (%) ^f		Refs.
			Procedure ^d	Technique ^e	Concentration range	Det. limit	Operational	Storage	
SKBR-3 cells	EAD/dip-coating	GCE/mesop. SiO ₂ /CS-luminol/HER-2 AB	Immunosensor Acc. – Det.	ECL	20–2000 cells mL ⁻¹	20 cells mL ⁻¹	5 me. (RSD = 1.6%)		250
Sucrose (in food)	LbL-EAD	SPCE/MnO ₂ /SiO ₂ /GO _x +Inv	EC	CV	0.017–0.342 mg mL ⁻¹	0.006 mg mL ⁻¹	4 me. (RSD = 4%)	1 month	213

^a Abbreviations: AFB1, Aflatoxin B1; BCR/ABL, mutated breakpoint cluster region protein; SKBR-3 cells, metastatic breast cancer cells.

^b Abbreviations for biocomposite silica-based film preparation procedures: EAD, electrochemically assisted electrodeposition; LbL, layer-by-layer; ED, electrophertic deposition; Stöber, Stöber growth method.

^c Abbreviations: GCE, glassy carbon electrode; IL, ionic liquid; AFB1 AB, Aflatoxin B1 antibody; GE, graphite electrode; AuNP, gold nanoparticle; Fc-MB, ferrocene-labeled molecular beacon; SPCE, screen printed carbon electrode; ChOx, choline oxidase; MWCNT, multiwall carbon nanotubes; DSDH, D-sorbitol dehydrogenase; MWCNT-Os, multiwall carbon nanotubes wrapped with a Osmium polymer; PEI, poly(ethylene imine); DI, diaphorase; NADGPS, nicotinamide adenine dinucleotide covalently bonded to glycidopropylsilane; CS, chitosan; PMG, poly(methylene green); PEI-Fc, ferrocene-functionalized poly(ethylene imine); PVA4VP, poly(vinyl alcohol – 4-vinylpyridine); ADH, alcohol dehydrogenase; PSS, poly(styrene sulfonate); PSSG, partial sulfonated (3-mercaptopropyl)-trimethoxysilane sol–gel; CSPE, carbon screen-printed electrode; PVA, poly(vinyl alcohol); GO_x, glucose oxidase; APTES, 3-aminopropyltriethoxysilane; Hb, haemoglobin; ITO, indium tin oxide; GDH, glucose dehydrogenase; Hap, hydroxyapatite; HRP, horseradish peroxidase; RGO-CD, reduced graphene oxide nanosheets with cyclodextrine; ADA, adamantane carboxylic acid; CPE, carbon paste electrode; DTAB, dodecyltrimethylammonium bromide; PANI, polyaniline; CE, carbon electrode; RTIL, room temperature ionic liquid; GNRs@SiO₂, silica coated gold nanorods; Mb, myoglobin; MSFs@Ru-Aptamer, mesoporous silica film loaded with Ru(bpy)₃²⁺ and capped with aptamer; Malt, maltase; mesop. SiO₂, mesoporous silica; HER-2 AB, human epidermal growth factor receptor 2 antibody; PGE, pyrolytic graphite electrode; Inv, invertase.

^d Abbreviations: Acc., accumulation; Det., detection; EC, electrocatalysis; Inh, inhibition.

^e Abbreviations: EIS, electrochemical impedance spectroscopy; ECL, electrochemiluminescence; A, amperometry; CV, cyclic voltammetry.

^f Expressed as % of remaining response (in parentheses) after a number of measurements (me.) or minutes/hours (min/h) of use (operational stability) or as RSD (relative standard deviation), or the given period of storage.

Figure captions

Figure 1. (A) Schematic illustration of the various coating methods applied to deposit sol-gel-derived silica layers on electrode surfaces. (B) The various ways to modify these layers in the form of hybrids and composites: (a) co-condensation route to organic-inorganic hybrids; (b) entrapment of biomolecules, nano-objects, or as interpenetrated silica-organic polymer; (c) the template route to nanostructuring and functionalization of the mesoporous films.

Figure 2. (A) Vertically oriented mesoporous silica films prepared by electrochemically assisted self-assembly (EASA): (a) schematic illustration of the EASA process; (b) TEM images of the ordered and oriented mesoporous silica film (b₁ top view with electron diffraction pattern as inset; b₂ cross-section, *reproduced with permission from ref. [60], Copyright 2007 Nature Publishing Group*); (c) Typical GI-XD pattern confirming the hexagonal packing of vertically aligned mesopore channels (*reproduced from ref. [61], Copyright 2009, with permission from American Chemical Society*); (d) FE-SEM micrograph obtained for a film generated by EASA on ITO electrode (the inset is an enlargement of the cross-sectional view obtained after vertical cleaving of the sample, *reproduced from ref. [60], Copyright 2007, with permission from Nature Publishing Group*); (e) TEM micrographs of electrogenerated multilayer mesoporous thin films prepared by sequential EASA (bottom: cross-section views of a four-layer film: top: a magnified view at the intersection between two electrodeposited layers in which white dashed lines represent the interlayer domain and the red ones illustrate the pore orientation maintained in both sides of the interface; arrows indicate silica wall and channel, *reproduced from G. Giordano et al., Electrochim. Acta 2017, 237, 227-236, Copyright 2017, with permission from Elsevier*); (f) an illustration of the electron hopping charge

transfer mechanism in a ferrocene-functionalized silica nanochannel (*reproduced from ref. [36], Copyright 2021, with permission from Elsevier*). **(B)** Silica nanochannel membranes generated by the Stöber solution spontaneous growth method: (a) schematic illustration of the process; (b-e) TEM images of the films deposited on glass ((b,c) cross-sections, (d,e) top-views, with insets in (c) and (e) representing the structural models of the cross-section and surface of the mesoporous silica film, respectively, *reproduced from ref. [66], Copyright 2012, with permission from Wiley-VCH Verlag*).

Figure 3. **(A)** Illustration of the various ways to deposit molecularly imprinted silica (MIS) films on electrodes (*reproduced from ref. [96], Copyright 2022, with permission from Elsevier*). **(B)** Schematic representation of the molecularly imprinted electrochemical sensor constructed for the detection of chlorogenic acid (CGA) by deposition of a molecularly imprinted silica (MIS) film a gold electrode surface pre-treated with (3-mercaptopropyl)trimethoxysilane (MPTMS); MIS was obtained by the sol-gel process from a solution constituted by tetraethoxysilane (TEOS), phenyltriethoxysilane (PTEOS), 3-(aminopropyl)trimethoxysilane (APTMS) and CGA (*reproduced from ref. [102], Copyright 2011, with permission from Elsevier*). **(C)** Schematic representation of the preparation a MIS sensor for L-phenylalanine based on a carbon electrode covered with a polyaniline (PAN) layer subsequently modified with β -cyclodextrin (β -CD)-incorporated multi-walled carbon nanotube (MWNT), and overcoated with an imprinted silica sol-gel film entrapping the target analyte (*reproduced from ref. [106], Copyright 2011, with permission from Elsevier*). **(D)** Left: illustration the fabrication of a molecularly imprinting sol-gel hybrid film on glassy carbon electrode (GCE) by the one-step electrodeposition of chitosan (CS), phenyltrimethoxysilane (PTMS), *in situ* formed gold nanoparticles (AuNPs) and template *p*-nitrophenol (*p*-NP). Right: selectivity revealed by differential pulse voltammetry responses of four nitrophenols (*p*-NP, *o*-NP, *m*-NP, and 2,3-diF-*o*-NP), measured with the

imprinted (black bars) and non-imprinted (gray bars) hybrid film modified GCEs at the individual characteristic oxidation potentials in their reduced states (*Reprinted from ref. [114], Copyright (2013), with permission from The Royal Society of Chemistry*).

Figure 4. Illustration of the various electrochemical sensing applications involving composite electrodes elaborated from continuous ordered mesoporous silica thin films, respectively with filled pores, open pores and functionalized pores.

Figure 5. (A) Planar screen-printed electrode configuration (three-electrode cell) and (B) schematic view of its modification with a silica biocomposite film (*reproduced from ref. [221], Copyright 2012, with permission from Wiley-VCH Verlag*). (C, D) Schemes of biocomposite films on electrode, with either (C) only the protein (Enzyme) or (D) or both the protein and nanoparticles (NP) encapsulated inside the silica matrix. (E) AFM images of the surface of glassy carbon electrode, respectively (a) before and (b, c) after modification with (b) SiO₂ and (c) SiO₂-Hb (c) biocomposite film (*reproduced from ref. [40], Copyright 2007, with permission from Elsevier*).

Figure 6. (A) Schematic illustration of (A₁) the preparation of aptamer-capped Ru(bpy)₃²⁺-loaded mesoporous silica films (MSFs) modified ITO electrode (Apt-Ru@MSFs/ITO) and (A₂) Apt-Ru@MSFs/ITO-assisted ECL aptasensor platform for target detection (*reproduced from ref. [222], Copyright 2016, with permission from American Chemical Society*). (B) Detection of the dehydrogenase enzymatic substrate: (B₁) illustration of the electrochemical pathway used for the co-immobilization of D-sorbitol dehydrogenase (DSDH) and diaphorase (DI) enzymes with ferrocene-functionalized poly(ethylene imine) (PEI-Fc) and the covalently attached cofactor NAD⁺ with the aid of glycidopropyl trimethoxysilane (GPS); (B₂) Amperometric responses obtained at an applied potential of 0.4V using GCE/(TEOS+GPS)/(DSDH+DI)/NAD-GPS/PEI-Fc (*i.e.*, with GPS) and

GCE/(TEOS)/(DSDH+DI)/NAD⁺/PEI-Fc (*i.e.*, without GPS); measurements have been performed for 14 h oxidation under convective conditions in 0.1 M Tris–HCl buffer (pH 9) containing 2 mM D-sorbitol (*reproduced from ref. [217], Copyright 2012, with permission from Elsevier*). (C) Illustration of the main approaches used for electrode modification with silica-based biocomposite films: (a) one-step entrapment of proteins and nanoparticles, (b) two-step modification by formation of a porous silica film and subsequent binding of biological nano-objects, and (c) electrodeposition of a first nanoparticles layer covered with silica biocomposite film. (D) Bioelectrocatalytic detection of H₂O₂ and nitrite: (D₁) scheme of GCE modification with silica-coated gold nanorods (GNRs@SiO₂), myoglobin and ionic liquid (RTIL); (D₂) CVs of the modified electrode in the presence of H₂O₂ at different concentration ((a) 0, (b) 113.1 μM, and (c) 346.5 μM); (D₃) linear plot of catalytic current (*i*_{cat}) vs. H₂O₂ concentration (*reproduced from ref. [219], Copyright 2009, with permission from Elsevier*).

Figure 7. (A) Schematic illustration of ECL oxidative-reduction mechanism of Ru(bpy)₃²⁺ molecule and TPrA (*reproduced with permission from C. Venkateswara Raju, M. Sornambigai, S. Senthil Kumar, IntechOpen, 2022, doi:10.5772/intechopen.96819*). (B) Schematic illustration of (B₁) the fabrication and application of a MIP-ECL sensor for Ochratoxin A (OTA) and (B₂) the proposed self-enhanced ECL mechanism; the self-enhanced superstructures was constructed by successively loading N-doped graphene quantum dot (NGQDs) and CsPbBr₃ perovskite nanocrystals (PNCs) onto graphene supported two-dimensional mesoporous SiO₂ nanosheets (2D mSiO₂-G) prepared from TEOS and CTAB, and subsequently depositing a molecularly imprinted overlayer with high affinity for OTA (*reproduced from ref. [242], Copyright 2022, with permission from Elsevier*).

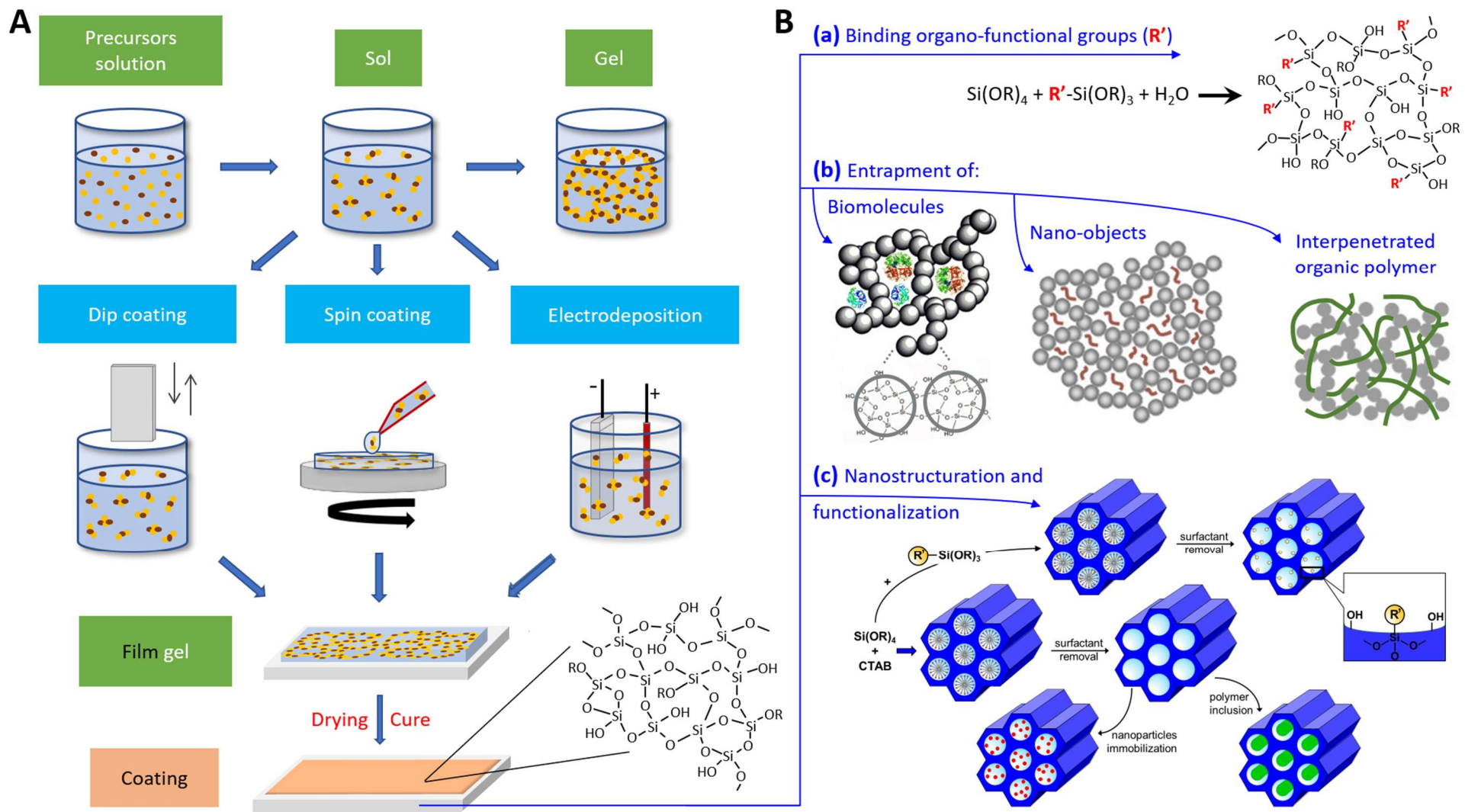


Figure 1

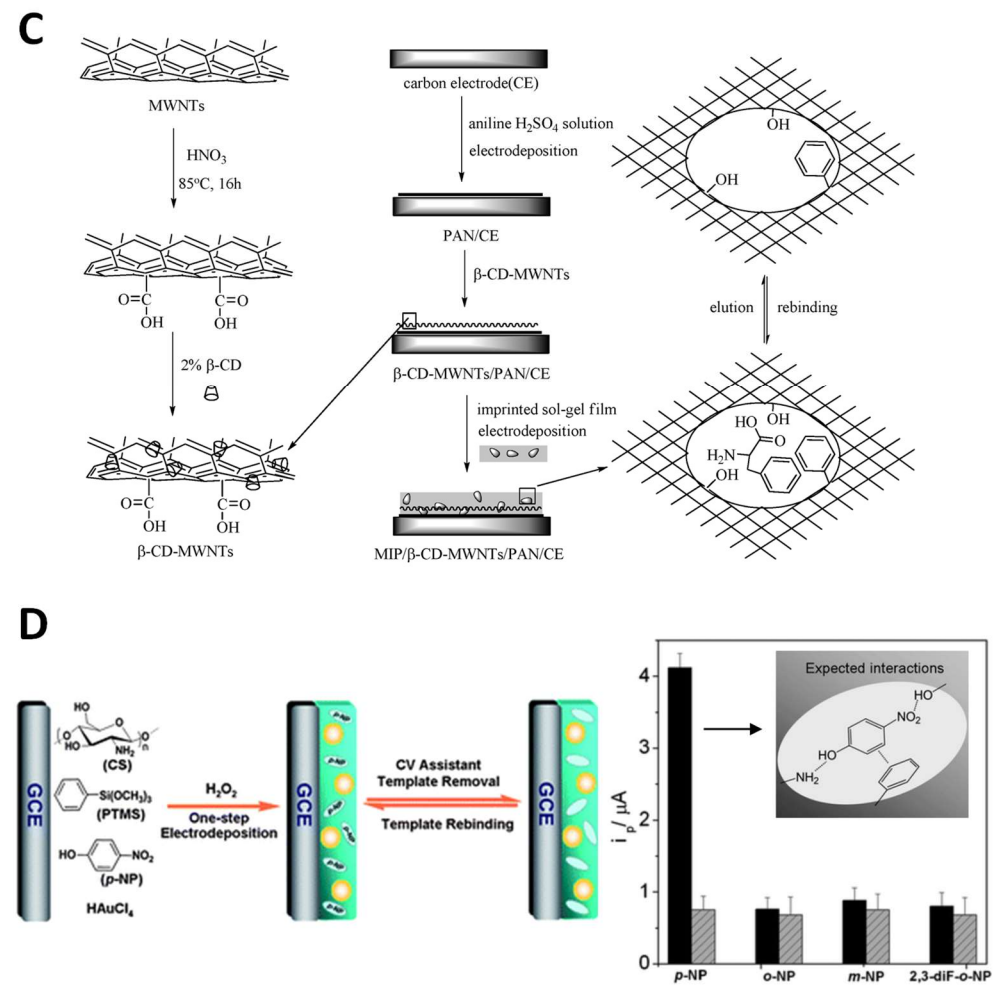
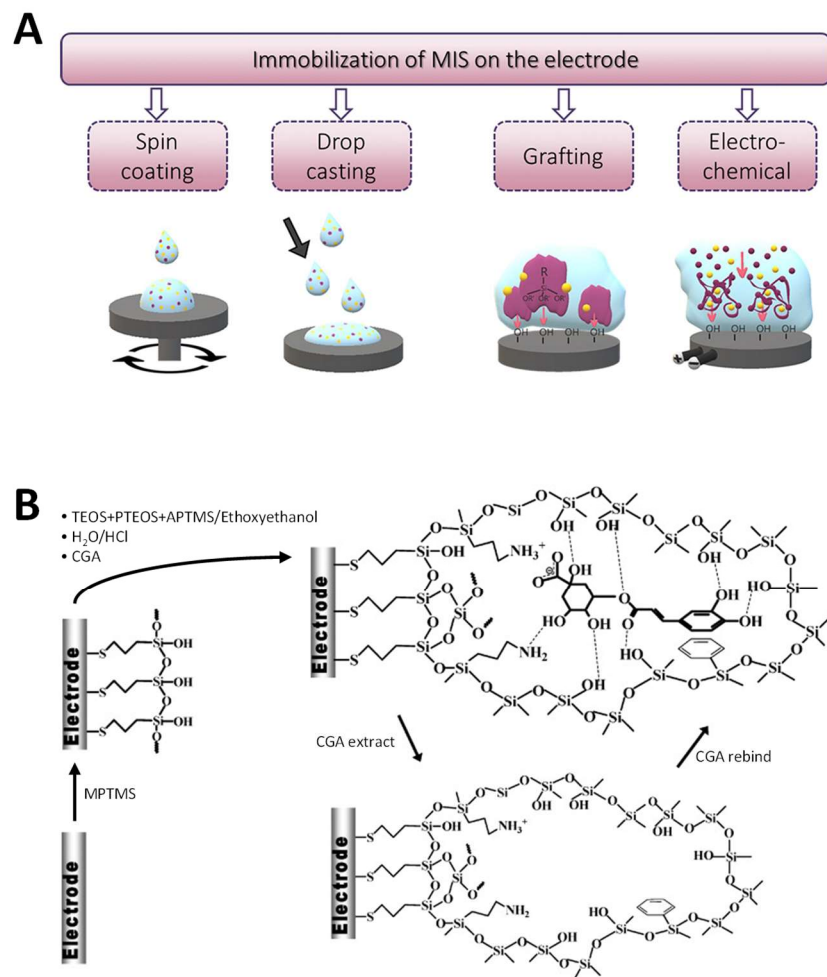


Figure 3

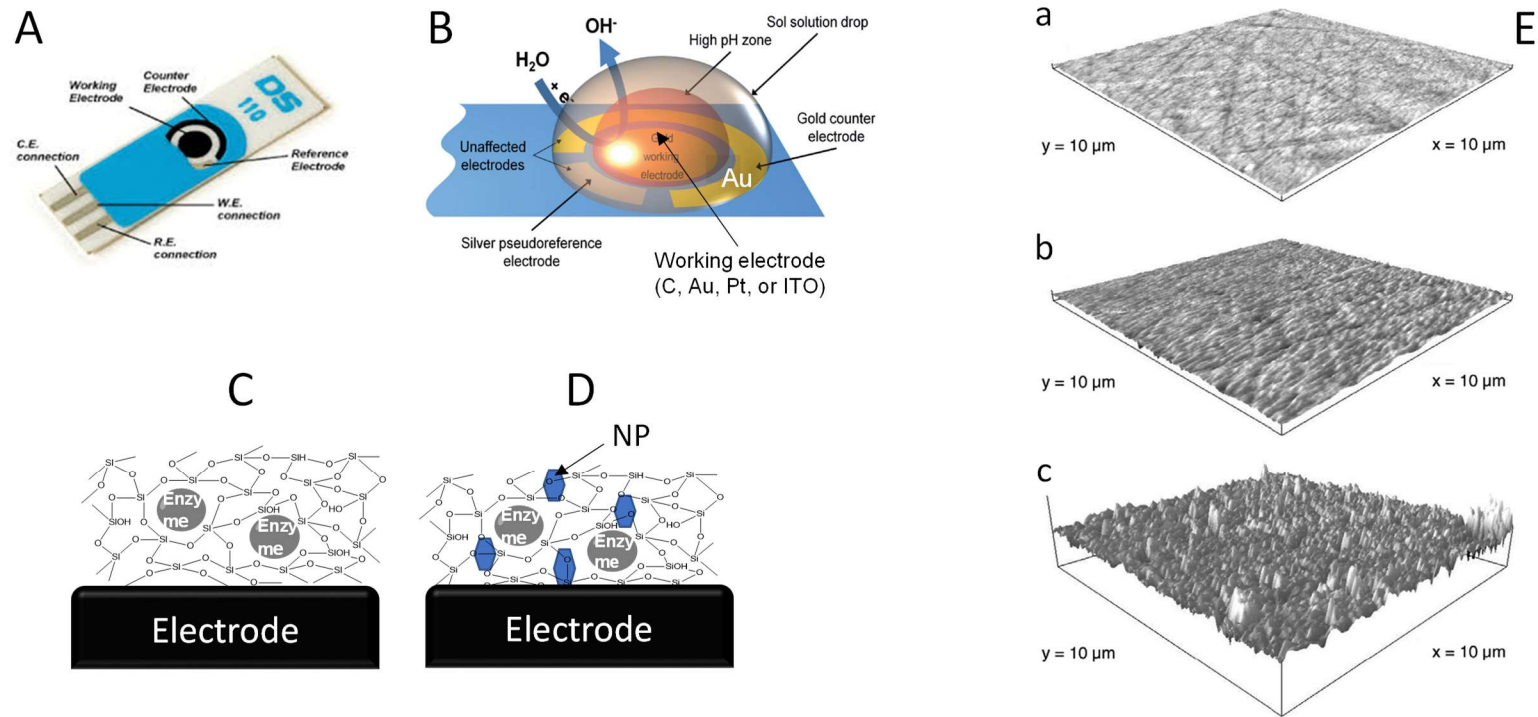


Figure 5

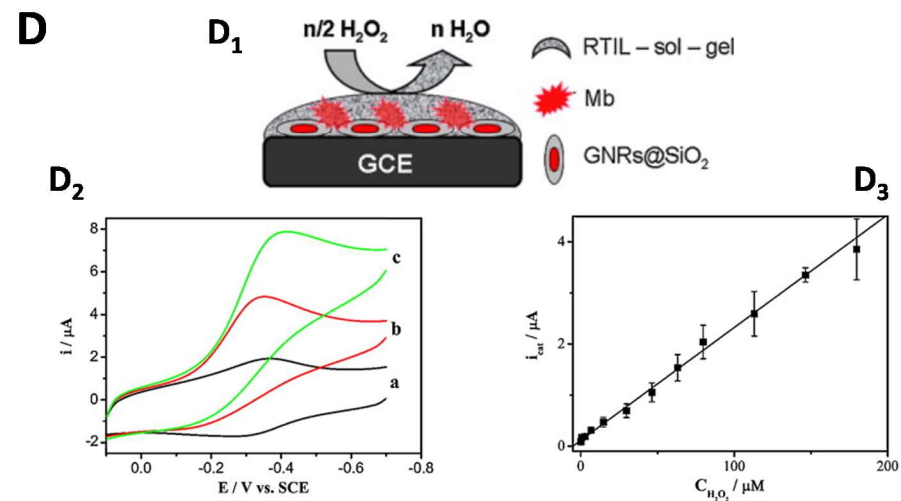
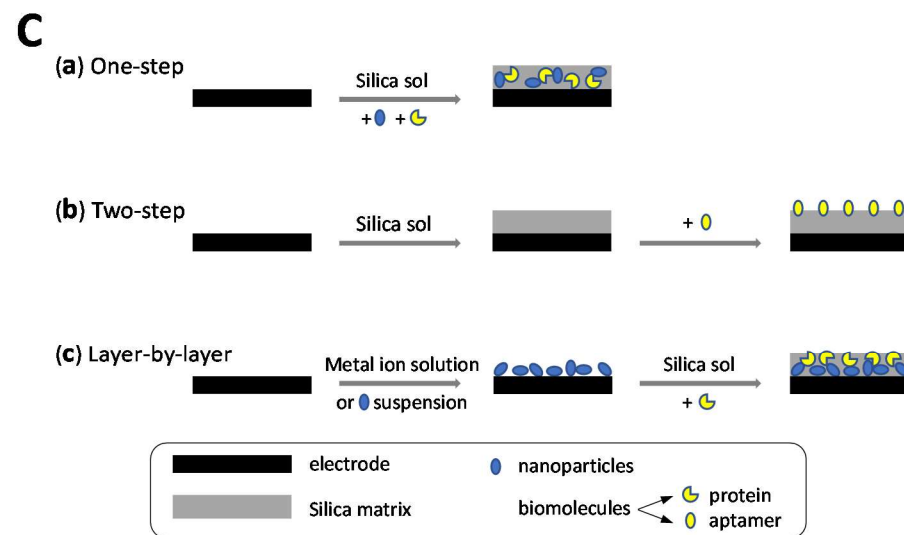
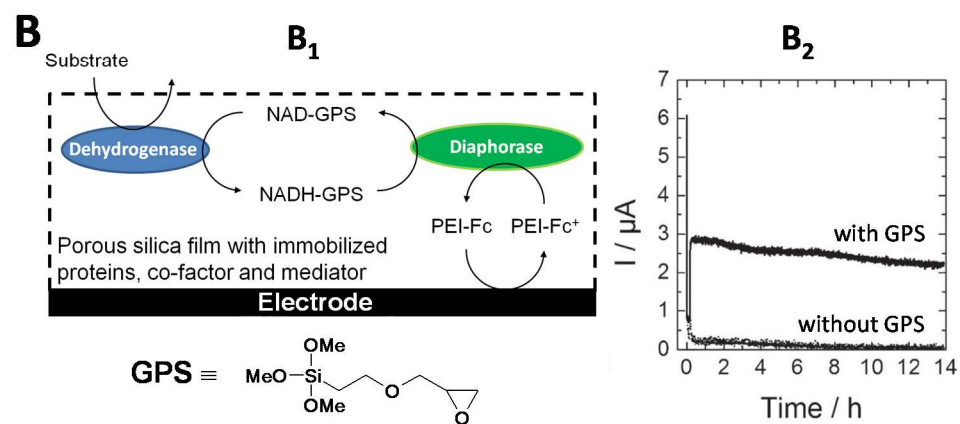
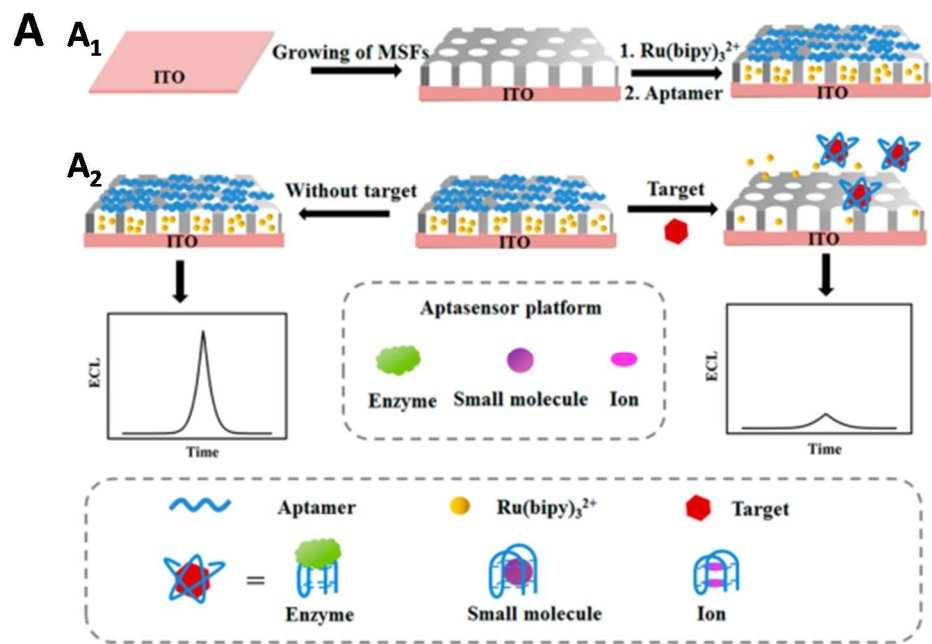


Figure 6

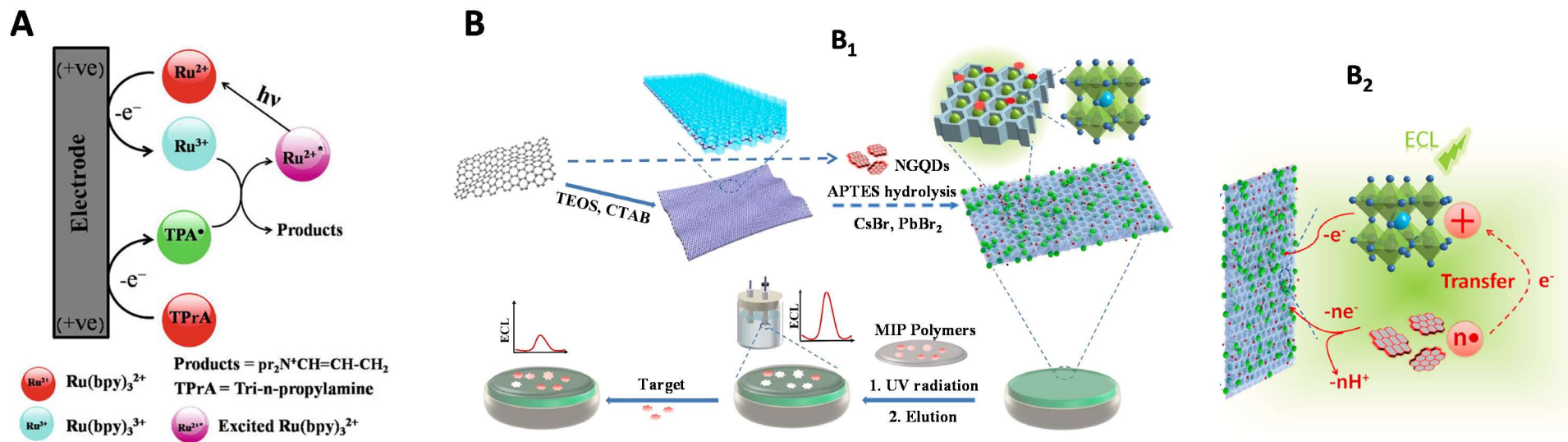


Figure 7