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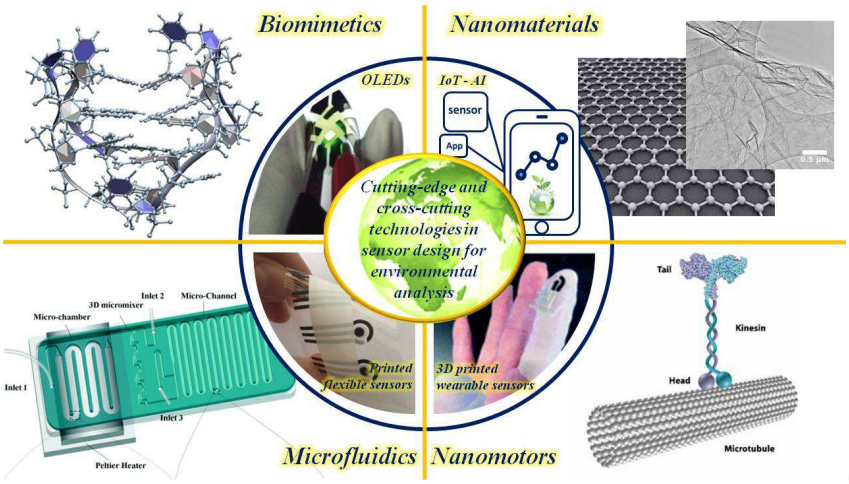
Graphical abstract



How Cutting-edge Technologies Impact the Design of Electrochemical (Bio)sensors for Environmental Analysis. A Review

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Abstract

Through the years, scientists have developed cutting-edge technologies to make (bio)sensors more convenient for environmental analytical purposes. Technological advancements in the fields of material science, rational design, microfluidics, and sensor printing, have radically shaped biosensor technology, which is even more evident in the continuous development of sensing systems for the monitoring of hazardous chemicals. These efforts will be crucial in solving some of the problems constraining biosensors to reach real environmental applications, such as continuous analyses in field by means of multi-analyte portable devices. This review (with 203 refs.) covers the progress between 2010 and 2015 in the field of technologies enabling biosensor applications in environmental analysis, including i) printing technology, ii) nanomaterial technology, iii) nanomotors, iv) biomimetic design, and (v) microfluidics. Next section describes futuristic cutting-

edge technologies that are gaining momentum in recent years, which furnish highly innovative aspects to biosensing devices.

Keywords: pollutants, printed (bio)sensors, nanomaterials, artificial bioreceptors, lab-on-a-chip

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1. Introduction

In the last decades, due the industrial globalization and the rise in population, the increasing amount of hazardous compounds that have high impact on human wellbeing and environmental health have been of increasing concern. These chemicals include heavy metal ions, pesticides, phenolic compounds, xenobiotics, and hydrocarbons to name a few. Over the past century, they have been widely disseminated into the environment and some of them have never undergone safety testing, and a minimal assessment has been provided on their potential toxicity or the possible synergistic effects of simultaneous exposures to multiple chemicals [1, 2].

Among these chemicals, emerging substances have received a huge attention because of their increasing presence in the environment, their potential threats to environmental ecosystems, and the absence of routine monitoring programmes at the European level. Due to their high relevance, these substances have been identified by the NORMAN Group (Network of reference laboratories, research centres and related organizations for monitoring emerging environmental substances) and enclosed in a list of priority substances, whose latest update was provided on February 2016 [3]. Emerging substances encompass a miscellaneous group of compounds, including pharmaceuticals and personal-care products, drugs of abuse and their metabolites, steroids and hormones, endocrine-disrupting compounds, surfactants, perfluorinated compounds, phosphate ester flame retardants, industrial additives and agents (e.g. benzotriazoles and benzothiazoles), siloxanes, artificial sweeteners, biocides, polar pesticides and their degradation products, and gasoline additives [4].

For these reasons, important pollution issues persist for several countries considering that the hazardous compounds represent an important risk for environmental and human health, food security, and ecosystem resilience. For example, the veterinary use of diclofenac, a human pharmaceutical used for anti-inflammatory treatment, has been found to be responsible for the massive decline in populations of vulture species in certain areas of Asia; ethinyl estradiol, an active ingredient of contraceptive pills, has been associated with endocrine disruption in fish; lastly, the

long-term exposure to antibiotics, used in human and veterinary medicine, may contribute to the selection of resistant bacteria in the environment which may have significant implications for human health [5].

Moreover, environmental pollution is nowadays recognized as a major cause of illness and mortality in both developed and developing countries, being responsible for 8.9 million deaths around the world each year according to the World Health Organization [6], and having great economic costs which burden on the national health care systems of countries around the world [7].

Therefore, there is an increasing demand to develop joint technological solutions for pollution monitoring and management. Undeniably, a holistic approach combining cutting-edge technologies in sensor development can envisage the construction and assembling of smart analytical tools able to characterize the extent of contamination at relevant spatial scales and in terms of its eco-effects, and to provide an inclusive and representative picture of the quality of the environment [8]. Indeed, while the presence and the effects of metals, bacteria, hydrocarbons, nitrates and ammonia in water have been described for several decades, the occurrence of phthalates, pharmaceuticals compounds, PAHs, PCBs, and Bisphenol A is often not available.

As extensively reviewed by Geissen and coworkers [9], there are several challenges regarding the detection of hazardous chemicals. Among them, spatial and temporal distribution is also important, since intra-day and inter-day variations, seasonality and occasional events can influence the attainment of a harmonised screening. In this context, the exploitation of conventional analytical techniques to monitor hazardous chemicals requires the collection of repeated spot sampling (time and cost consuming), their analyses done by laboratory set-up instruments, with the evaluation of the risks/effects, providing only snapshot data of contaminated areas without realistic information on spatio-temporal variations in the composition of real samples and their relative effects. Among standard techniques, chromatographic methods have provided reliable identification and quantification of compounds at ultratrace level, but their high cost and lack of portability for in field analysis are the major drawbacks. Moreover, obstacles related to classical technologies (i.e.

time and cost consuming repeated spot sampling, sample collection and transport, employment of skilled personnel, failing in providing data on global toxicity) could have detrimental implications in terms of regulatory analyses and accurate monitoring of environmental quality.

In this context, (bio)sensor technology allows to design ad hoc analytical systems which include a combination of advantages, in terms of reduced time-to-result; automation and miniaturisation, and consequently portable and user-friendly system platforms for in field high-throughput analysis; detection of a single analyte as well as simultaneous multi-analyte testing.

Furthermore, as stated by Escarpa et al. [10] "*with the appearance of advanced approaches such as screen-printed technology, biosensors, microchips and nanotechnology, among others, electroanalysis is undergoing a true Renaissance*", the last trends in electrochemistry, nanotechnology, biomimetic design, microfluidics, and microengineering have contributed to the development of a new generation of biosensors. Indeed, over the past decade, the number of publications describing the development of electrochemical (bio)sensors has exponentially increased. Several reviews on nanomaterial-based biosensors have also been published highlighting the prodigious performance of materials at the nanoscale. Similarly, (bio)sensing systems based on microfluidics and lab-on-a-chip technology have been broadly reported, due to their key contribution towards the development of compact analytical devices, able to perform on-line sample processing and continuous analysis, enhancing the selectivity of the response, improving detection limits, and avoiding interferences. In addition, the advances accomplished in recent years in biomimetic design and material science are leading to the development of smart and functional biohybrids tailored for stable and sensitive monitoring systems [10-13].

The aim of this review is to provide an exhaustive overview of the new convergence technologies for the development of innovative electrochemical (bio)sensors to monitor hazardous chemicals in different environmental compartments. The following paragraphs report an overview of the innovative and futuristic technologies, including printed technology, nanomaterial technology,

nanomotors, biomimetic design, microfluidics, and cross-cutting technologies which resulted very useful for (bio)sensor effective environmental applications.

2. Printing technology

Printing technology involves the deposition of several successive layers of conductor and dielectric layers on an insulating support using a number of processes including screen-printing and ink-jet approaches. This technology demonstrated its high potential in sensor fabrication by printing the electrochemical cell on different types of supports, such as polymeric and ceramic materials. The cells can consist of three electrodes (working, counter, and reference) in case of voltammetric and amperometric analyses or just of two electrodes in case of conductometric and potentiometric analyses. The working electrode defines the properties of the whole device and it can be printed using carbon, gold or silver based inks, which can be successively modified with nanomaterials, electrochemical mediators, and bioelements to improve the selectivity and sensitivity of the device. Considering the last trends in printing technology focalised on the development of innovative supports with special features in terms of sustainability and flexibility, as well as smart functional nanomaterials furnishing astonishing analytical performances as sensitivity and selectivity, section 2 will mainly focus on: i) printing techniques, ii) smart supports, and iii) technologies for working electrode modification with micro/nanomaterials described in literature for environmental analysis.

2.1 Printing techniques

At the same strength of electrochemical methods which helped in reducing the need of sophisticated instrumentations to conduct qualitative and quantitative analysis, printing technology also helped to obtain miniaturised, cost-effective, and flexible devices. Thus, bulky electrodes are being almost

entirely substituted by printed platforms which do not necessitate of cleaning treatments and, most important, are disposable and affordable.

Printing technology consists of different techniques (e.g. screen-printing, ink-jet, roll-2-roll, sheet-to-sheet) to offer portable and remote devices as effective and valuable alternatives (respect to the bulk electrodes) for rapid monitoring, particularly in the environmental field. Among these techniques, serigraphic printing, also known as screen-printing, is the most used for manufacturing printed electrodes, enabling a rapid method to provide mass-production.

Screen-printed electrodes have been widely used in the environmental field for the detection of several pollutants, including heavy metal ions, pesticides, and toxins to name a few. For instance, commercial screen-printed gold electrodes were employed for Hg(II) quantification by square wave anodic stripping voltammetry in waste and rain water samples, obtaining a good agreement with reference ICP-MS method [14]. Graphite based screen-printed electrodes were likewise exploited by Banks' group to detect phosphate, measuring the resulting molybdate based electroactive complex, allowing orthophosphates measurement with linear range up to 20 μg L^{-1} and a detection limit of 0.3 μg L^{-1}. This printed sensor was challenged in canal water samples providing data in accordance with ion chromatography and ICP-OES [15].

Although the above-mentioned advantages of screen-printing, its contact modality approach could produce large amounts of wastage (i.e. inks, solvents) and sometimes the requirements of finely micrometric sized electrodes could not be satisfied.

To this regard, the inkjet printing technique can be considered a valid noncontact alternative in electrode fabrication, thanks to its feasibility, reduced waste generation, and versatility. As reported in literature, inkjet-printed electrodes are almost entirely utilized as gas sensors in environmental field measurements. Dua et al. [16] reported the fabrication of a flexible and lightweight chemiresistor based on inkjet-printing of graphene oxide platelets. A flexible plastic support was chosen and chemically aggressive vapours (i.e. $CHCl_3$, CH_3OH, hexane, NO_2, and Cl_2) were detected by monitoring the variation of the device resistance. These compounds were detected at μg

L^{-1} level using an air sample at room temperature, without the aid of a vapour concentrator. Altenberend and co-workers [17] developed a fully printed capacitive gas sensor on flexible a PET support. They inkjet-printed silver nanoparticles formulation as drop-on-demand technique to develop a flexible platform for gas sensing, testing the humidity and evaluating the presence of three common volatile compounds such as propanol, ethanol and acetone. Authors claimed the long functionality and duration of this device that was investigated for over four months of sequential operation at a temperature, from 5 to 45 °C.

Merkoci and his group also demonstrated the suitability in utilizing the inkjet-printing to prepare a robust and stable Ag/AgCl pseudoreference electrode [18]. They evaluated the opportunity to fabricate a low-cost, disposable, and miniaturized reference electrode that showed good reproducibility thanks to the finely regulated inkjet-printing technique, easily extendible to various analytical fields. Recently, Jovic et al. [19] developed an electrochemical sensor for the detection of free chlorine in water samples, exploiting the features of the inkjet-printer to fabricate low-cost silver electrodes on a flexible polyimide-based foil. Linear sweep voltammetry was used to detect chlorine exploiting the spontaneous reaction between silver and free chlorine species present in solution (i.e. HClO and ClO^-). The level of free chlorine in water was quantified up to 100 mg L^{-1}, with a detection limit of 2 mg L^{-1}. Free chlorine was detected in swimming pool water samples and the inkjet-printed silver electrodes gave satisfactory results in good agreement with those obtained using the standard colorimetric DPD methodologies, with a recovery of 90% ca.

The gravure printing is also particularly attractive due to its optimal control of sensing layer thickness and ability to use a wide range of inks. Among them, roll-2-roll deposition allows an extremely high-resolution functionalization of flexible supports [20]. Huang et al. [21] utilized this technique to realize an ultraflexible NO_2 chemoresistor for the detection of environmental nitrogen dioxide from 0.5 to 50 mg L^{-1} in an air sample with a fast response of 12 s. Moreover, this sensor was particularly resistant to mechanical stress, being able to retain almost its entirely performance after ca. 1000 bending cycles.

Other methods for electrode fabrication, such as thin film deposition by sputtering and evaporation, have been also described by Kokkinos and Economou [22]. They microfabricated an electrochemical device constituted by successive sputtering silver, platinum, and antimony onto an oxidized silicon support, serving as reference, counter, and working electrodes. Lead and tallium ions were simultaneously detected by square wave anodic stripping voltammetry reaching a detection limit of 0.7 and 0.9 µg L^{-1}, respectively. The suitability of this sensor was tested with water sample that was, firstly, spiked with 5 µg L^{-1} of lead and 10 µg L^{-1} of tallium, then acidified and analysed, obtaining a recovery of 97 and 102%, respectively.

2.2 Smart supports

Besides electrode printing techniques, the production of printed sensors entails also the exploitation of smart supports including polyester, ceramic, and paper in order to enhance their affordability, robustness, and reproducibility. As an example, Hallam et al. [23] used a polyester flexible film to build a screen-printed electrode based on graphite ink able to detect heavy metal ion traces. This sensor was able to analyse real water matrices after acidification (pH = 1) without any further dilution or filtration, quantifying hexavalent chromium down to 19 µg L^{-1} in canal water.

A bismuth based sensor printed on polyester was realised for heavy metal ion detection by Neagu and co-workers [24]. In this case, this sensor was exploited to evaluate the phytoremediation efficiency of the aquatic macrophyte *Lemna minor* L., monitoring the presence of lead and cadmium before and after the phytoremediation process.

In addition to polyester, several other supports have been employed for screen-printing depending on specific necessities. For instance, Silwana et al. [25] prepared an analytical device using bismuth modified ceramic-based carbon SPE to detected platinum, palladium, and rhodium in aquatic environments. Fernandez and colleagues [26] prepared a sensor to trace mercury ions in many kinds of real water samples (i.e. river, industrial, and waste) using SPEs printed on ceramic support

modified with gold nanoparticles. A limit of detection of 0.2 µg L^{-1} in standard solutions was achieved, which resulted lower than the threshold established by EPA and the EU, which is respectively 2 and 1 µg L^{-1}. After the real matrices were spiked with 1 and 7 µg L^{-1} of mercury recoveries between 95% and 108% were attained. However, the samples required ice-bath, centrifugation, sonication, that limited real in-field applications.

Cerium and gadolinium ions have also been analysed by using these ceramic-based carbon SPEs, grafted with a double ion-imprinted magnetic nanoparticles [27]. These sensors were capable to detect simultaneously these two lanthanide ions by using differential pulse anodic stripping voltammetry, achieving a LOD of 0.07 and 0.19 µg L^{-1} respectively. Analysis of spiked wastewater, just diluted 10-fold to mitigate the matrix effect, was carried out obtaining recoveries close to 100%.

As stated before, many supports can be adopted for screen-printing, including glass fiber as reported by Li et al. [28]. They screen-printed a graphite-based electrode on a glass fiber for the simultaneous detection of hydroquinone, catechol, and resorcinol, enhancing the performance of the SPE by decorating it with gold nanoparticles and multi-walled carbon nanotubes (MWCNTs). These isomers of dihydroxybenzene were detected at the level of 0.1 µM. Real samples of tap and river waters were analysed obtaining satisfactory recoveries between 96% and 105%.

As evidenced by these examples, the suitability of the electrodes to be screen-printed on various supports, ranging from plastics to ceramic, and glass fibers, was largely highlighted in many environmental matrices. However, the electrodes printed onto plastic supports have demonstrated to achieve larger success with respect to others typologies, because of their flexibility and superior resistance to strain. Many of these platforms, thanks to their own properties, have also shown their fittingness to be embedded in automatic flow systems, toward the realization of de-centralized analysis sites [29-31].

Moreover, screen-printing technology allows mass-producing electrodes in platforms, usable as a one-shot sensor or reusable many times if properly modified. Considering the selection of the most

appropriate support on which the electrode is printed, this formidable technology is moving toward the use of even more ultraflexible supports in order to assemble "outside" of laboratories. Wang research group demonstrated the suitability of electrodes to be screen-printed onto GORE-TEX to create one of the first examples of wearable sensor [32]. They carried out measurements towards the detection of nitroaromatic explosives, and the water-proof properties of the GORE-TEX allowed the sensor to be favourably comparable to those printed on cotton or polyester. DNT and TNT explosives were readily detected in vapour phase at mg L^{-1} levels. Furthermore, they examined the influence of laundry washing, and strain. These sensors were used for up to nine consecutive measurements and after three laundry cycles, where 50% of the GORE-TEX fabric-based sensors maintained their sensing features.

Further, the same group screen-printed a graphite-based electrode onto a rubber neoprene wetsuit (Figure 1A) [33]. This sensor directly detected the presence of environmental pollutants, such as heavy metal ions (i.e. copper) and nitroaromatic explosives (i.e. TNT) in seawater samples. Detection in the µg L^{-1} range for both analytes tested was possible, allowing the wearer to in situ monitor the level of environmental pollutants while performing other tasks, with no time loss due to treating sample. Inspired by the possibility to the "skip-the-lab" approach, they fabricated a Forensic Finger by screen-printing electrodes directly on a nitrile glove [34] (Figure 1B) able of sampling and sensing the analytes in few minutes, and producing distinct voltammetric fingerprints specific to both gunshot residues and explosives. The conductive media was assured by the use of a solid ionogel electrolyte that eliminated any sample treatment and liquid management. As claimed by the authors, this ultraflexible support avoided the sensor to compromise its analytical performance after the repeated mechanical stress, making it a useful device in the crime scene investigation scenarios.

2.2.1 Paper-based electrodes

We choose to dedicate an entire section to an extremely important support, which gained momentum in the last few years in printed electrode fabrication: paper. Depending on the type of paper involved, it has been possible to realize many platforms exploiting all the advantages of using these cellulosic supports. Hydrophilicity, porosity, high-surface area, affordability, and sustainability are just some of the features that made paper an appealing support in diagnostic device development. Similar to “printing”, which kinds of paper are we interested in? The answer is: all kinds. In electrochemical devices fabrication, the most popular paper is the Whatman No.1 due to its smooth surface, structural uniformity, and absence of additives. Besides this highly sophisticated paper, other grades of chromatography, filter, blotting, and office paper can be utilized depending on the application. In recent years, the research groups headed by Professors Whitesides and Henry have been the most experienced in the development of paper-based platforms, both electrochemical and colorimetric [35, 36]. Following their guidance, many groups decided to develop such kind of paper-based platforms, exploiting their active properties and availability. The rationale in using filter paper as a support is represented by its capacity to load reagents. All the reagents necessary for an analytical assay can be rationally confined in a zone of the paper. To do this, specific procedures for the creation of hydrophobic barriers are required. The most used are wax-printing and photolithography, but also inkjet printing and oxidative plasma are exploited treatments to create these kinds of delimitated hydrophilic areas. Cinti et al. [37] also combined the effectiveness of screen-printing with wax-printing to realize an all-in-one paper-based phosphate sensor (Figure 1C). They used a less-sophisticated filter paper to cover the laboratory bench, and transferred the reference colorimetric method for the detection of phosphate in water directly into the paper support. All the reagents necessary to carry out the detection were pre-loaded onto the test area (where electrodes will be screen-printed): molybdate and chloride ions in strong acidic conditions. They screen-printed a 5% (w/w) carbon black-containing graphite ink and detected

phosphate in a wide range up to 300 μM with a limit of detection of 4 μM. In this work, the authors took advantage of the outstanding filter properties of paper obtaining good recoveries (96 ± 10%) in non-treated spiked river water.

A similar configuration was described by Medina-Sánchez et al. [38] in developing a lateral flow paper-based sensing device for lead and cadmium ions detection in environmental matrices. They screen-printed 500 μm-width electrodes, graphite ink formed the working and counter electrodes, while Ag/AgCl was printed as a reference electrode on a waxed chromatographic paper. Acetate buffer and surfactant were preliminary drop cast at the beginning of the channel paper and then the sample was analysed. With this procedure, lead and cadmium ions were quantified in aqueous samples in a range comprised between 10 and 100 $\mu g\ L^{-1}$, achieving limits of detection of 7 and 11 $\mu g\ L^{-1}$, respectively. They analysed these pollutants in complex matrices (i.e. seawater and mud), highlighting the possibility to perform analysis without the need of sample pre-treatment thanks to the filter capability of the paper. Also Henry's group realized a paper-based device to detect lead and cadmium ions [39] (Figure 1D). They took advantage of paper as support for sample collection and reagent loading. They utilized a SPE on polyester which was integrated in a paper box. The working electrode was made using an ink modified with a mixture of MWCNTs, graphite powder, and carbon ink. Under the optimized conditions, the anodic stripping voltammetry allowed the detection of lead and cadmium ions in the range of 5-150 $\mu g\ L^{-1}$, with a detection limit of 1 $\mu g\ L^{-1}$ for both the heavy metal ions. The paper disk was capable to pre-concentrate the airborne particulate matter as evaluation of the exposure to air pollution. Paper disk filter was digested by acidic treatment and microwave, and then a single drop of buffer was sufficient to allow the detection of the two ions at the electrode surface. Even if this method does not involve a direct printing onto a paper support, it shows how the porosity and surface area of paper could readily be adopted in an electroanalytical test.

Nurak et al. [40] utilized a spraying method based on lacquer for the fabrication of a paper-based device toward nickel ion detection in wastewater. They chose a Whatman No.4 filter paper where

hydrophobic area was created by spraying lacquer on filter paper, while the hydrophilic area was protected by a mask made of iron. Carbon and Ag/AgCl inks were screen-printed over the hydrophilic area, respectively forming the working/counter and reference electrodes. Under the optimized conditions, detection was linear from 1 to 50 mg L^{-1} with a detection limit of 0.5 mg L^{-1}. Then, nickel ions were detected in wastewater sample of a jewellery factory after the matrix was filtered, acidified, heated, and fortified with all the electrolytes necessary for the ASV analysis. Nickel ions were recovered at the 95% confidence level compared also with inductively coupled plasma optical emission spectrometry measurements. The authors asserted that this procedure could resolve the issue related to the classical wax-printing approach due to wax spreading. The advantages of acrylic resin, obtained by applying a polymerization, are water resistance, good adhesion, and fast drying.

Paper was also chosen as smart support in the fabrication of potentiometric-based electrodes as described in 2014 by Whitesides' group, which realized an electrochemical paper-based analytical device by integrating a small ion-selective paper electrode and a paper reference electrode for potentiometric measurements of K^+, Na^+, and Ca^{2+} in aqueous solutions [41]. They exploited wax-printing in order to create hydrophobic barriers around the sample and reference zones. After 10 μL of solutions wet the printed electrode, K^+, Na^+, and Ca^{2+}, were detected linearly ranging between 10^{-4}- 10^{-1} M, 10^{-3}- 1 M, and 10^{-4}- 10^{-1} M, respectively. They fabricated up to 29 devices onto a page of chromatography paper (Whatman No.1) making an easy adaptable platform for measuring relevant ions in environmental matrices. Despite the easiness of the potentiometric measurements, the authors affirmed that the stability of the device appeared to be lower with respect to the conventional devices, because of the drift of the measured potential (several millivolts in minutes). In the same year, Mensah et al. [42] exploited the superior adsorbent properties of filter paper to prepare a conductive substrate. They impregnated this support with a dispersion of single-walled carbon nanotubes (SWCNTs). Gold was chosen as material for printing the electrode and it was sputtered onto the treated paper. After these treatments, the paper-based electrode was modified

with a mixture of ion-selective membranes for the detection of cadmium, silver, and potassium ions, with detection limits of 1.2, 25.1, and 11 nM, respectively. These universal protocols for ion selective electrode fabrication were conceivable thanks to the special features of paper, which allowed a rapid and quantitative adsorption with the conductive carbon nanotubes. Metters et al. [43] demonstrated the suitability in utilizing office paper instead of polyester in sensor fabrication. They screen-printed a graphite-based ink for the detection of nitrite ions. The limit of detection was 15.1 μM and the authors highlighted how the use of the paper-based screen-printed sensors was totally competitive with the traditional plastic-based ones in terms of analytical performance and stability. This platform was used to detect nitrite directly in canal water, finding a perfect overlay between the calibration curves in the real matrix and in the buffered solution. De Araujo and Paixao [44] fabricated an electrochemical device for different applications, directly on office paper by screen-printing working, counter, and reference electrodes with silver ink using cyclic, square-wave anodic stripping and differential pulse voltammetry as measurement techniques. They claimed that the use of office-paper instead of the widely used chromatographic paper (Whatman No.1) allowed reducing the fabrication cost by 96%. By combining screen-printing and wax-printing for paper-area delimitation, they quantified lead, chloride, and picric acid, estimating an average time of 1 h to fabricate 72 electrochemical sensors. Picric acid, lead, and chloride were detected down to 30, 1.7, and 7 μM, respectively, demonstrating the suitability to fabricate a general-concept platform with a poor laboratory setting.

The extraordinary features of paper have been also exploited in the development of devices for gas phase monitoring. To this aim, Dossi and co-workers [45] developed a gas sensor by soaking a filter paper with ionic liquid and screen-printing carbon ink doped with cobalt phthalocyanine. They adopted a wax printer to define a circled-working area for the detection of 1-butanethiol vapours in a flow injection analysis configuration. Thanks to a careful control of the preparation procedure and to the ability of cobalt phthalocyanine to electrocatalyze thiol oxidation, they detected the model gas down to 0.5 μM. The chromatographic paper guaranteed a close contact between gas phase and

the electrochemical detector, allowing a faster diffusion of the analyte when compared to that of a liquid phase system.

In their work, Hu et al. [46] established a simple procedure for employing inkjet printing, to obtain a mass production of nanoporous gold electrode arrays onto a cellulose membrane. After they accurately evaluated the deposition of electrodes, the use of ionic liquids as the electrolyte media allowed the sensor to detect oxygen in air. The recorded current decreased in the range of 0.054−0.177% oxygen, reaching a detection limit of 0.0075%. With this procedure, they inkjet-printed more than 200 patterns of electrode arrays onto a 10 cm-cellulose membrane in less than 30 minutes.

2.3 Technologies for working electrode modification with micro/nanomaterials

In the previous subsections, different methods and supports have been discussed for electrode fabrication. In this subsection, the importance of electrode modification as a crucial step to improve selectivity, sensitivity, and accuracy of sensors has been highlighted, describing key examples from the literature of different techniques to modify printed electrodes.

A conventional technology to produce screen-printed electrodes modified with nanomaterials consists in the use of inks already containing nanomaterials, thus avoiding further steps of fabrication [47]. For example, Noyrod et al. [48] developed an electrochemical sensor using graphene modifier directly introduced in the carbon-ink, for the simultaneously detection of isoproturon and carbendazim. This in-house inclusion of graphene into the ink allowed obtaining better-defined peaks, higher sensitivities, and a lower oxidation potential with respect to the bare SPE. The proposed electrochemical platform was applied in spiked samples of river, rice-field water, and soil, and after extraction, resolvatation in ethanol, and dilution in $HClO_4$, the analytical results revealed recoveries for isoproturon and carbendazim in the range of 92.1-107% and 82.2-85.5%, respectively. The authors compared these results with those obtained with HPLC, revealing

no significant difference between the two methods. Cobalt phthalocyanine-contained carbon ink has been also exploited to fabricate working electrode of SPEs by Yoon et al. [49], which used this kind of electrode to develop a microfluidic chip for nerve agent detection. The cobalt phthalocyanine was capable to oxidize at low potential (ca. 0.1 V vs. Ag/AgCl) the enzymatic thiocholine by-product. The authors highlighted the feasibility of this portable biosensor microchip device for the detection of different acetylcholinesterase inhibitors.

While some electrodes have been modified employing modifiers directly in the ink in the stage of screen-printing, a diverse approach entails the deposition of modifier dispersions on the working electrode surface by inkjet-printing, providing a finest control of the surface modification.

The advantages of this strategy reside in a more efficient use of the material, high patterning, and the possibility to control the thickness of the modifier layer. For example, Tseng et al. [50] modified an interdigitated gold electrode by involving the use of an inkjet-printer to fabricate a PEDOT:PSS active layer. The fabricated platform was utilized in the assembling of a conductimetric gas sensor capable to detect CO_2 at the level of mg L^{-1}. Cinti and colleagues [51] inkjet-printed many layers of Prussian Blue nanoparticles onto a screen-printed carbon electrode in order to obtain a sensible and reproducible platform to detect hydrogen peroxide in many fields of applications. This technique allowed the successively deposition of 20 layers of PB nanoparticles on different electrodes with high reproducibility (i.e. relative standard deviation lower than 5%). This amperometric sensor was able to reliably quantify hydrogen peroxide in a wide range up to 4.5 mM with a detection limit of 0.2 μM.

Among surface modification techniques, electrospinning is another effective procedure to modify electrodes. This method produces continuous fibers of nano/microsized polymers and shows a large specific surface area, high porosity, and great mechanical resistance of the electrospun fibers [52]. Promphet et al. [53] electrospun graphene/polyaniline/polystyrene nanoporous fibers onto a carbon-based SPE for simultaneous determination of lead and cadmium ions in river water. The presence of these fibers allowed the response to increase 3-fold with respect to the unmodified SPE. Under

optimal conditions, lead and cadmium were detected respectively down to 3.3 and 4.43 µg L^{-1}, and thanks to the strain resistance of the fibers, these electrodes were used more than 10 times with a relative standard deviation < 5%. River water samples were digested by using a nitric acid, boiled on a hot plate, and adjusted with supporting electrolyte of 0.1 M HCl. After spiking treated samples, the % recoveries for lead and cadmium ions were found in the range of 85-109% and 95-104%, respectively.

An attractive alternative procedure to modify electrodes is the electrospray printing which allows, via electro-hydrodynamic jetting, to precisely control the film properties of the sprayed solution/dispersion. Furthermore, this method is very easy to custom-built and does not require particular equipment. Taylor and Velasquez-Garcia [54] realized a conductometric gas sensor to detect ammonia. They electrosprayed an ultrathin film made of graphene oxide nanoflakes on a 100 nm thick gold film obtained by means of electron beam evaporation. The developed device successfully detected ammonia down to 500 mg L^{-1} at room temperature, demonstrating its suitability in industrial processes surveillance.

Electrodeposition is another successful approach to modify printed sensors as highlighted by Calvo Quintana et al. [55] that have electrodeposited Bi film onto SPE previously modified with Nafion. A comparative study using *in situ*, *ex situ* and *bulk* procedures to modify SPE with Bi was carried out, demonstrating that the *in situ* approach allowed to detect Pb^{2+} reaching a lowest detection limit (0.15 µg L^{-1}). A graphite-based screen-printed electrode modified by using electrodeposition of Bi was also reported by Merkoci's group for phenol detection [56]. In detail, MWCNTs modified SPE was used to electrodeposit Bi-film and mushroom tissue by applying a deposition potential of -1.0 V. This tissue biosensor was investigated in synthetically prepared wastewater achieving recoveries of about 92%. Beside Bi, an *in situ* electrodeposition was also reported exploiting antimony to develop a sensor able to simultaneously detect Cu(II), Cd(II), and Pb(II) ions using differential pulse anodic stripping voltammetry, demonstrating its suitability in certified reference groundwater.

This sensor overcame the drawback of Cu(II), which is a relevant interference if using Bi based sensor [57].

Despite the high performing methods reported above, the drop casting approach, which merely relies on the drop-casting of the modifier dispersion onto the working electrode surface, stands as the most used technique. For instance, a graphite-based SPE was modified by drop casting with a dispersion of carbon black and gold nanoparticle nanocomposites to determine As(III) using linear sweep-anodic stripping voltammetry directly in drinking water, upon acidification with HCl. This device showed a linear detection range from 2 to 30 µg L^{-1}, with quantitative recovery values on water spiked with 10 and 20 µg L^{-1} As(III) [58]. This drop cast sensor was also exploited for inorganic mercury(II) ions at ppb levels in acidified river water and extracted soil using square wave-anodic stripping voltammetry [59].

3. Nanomaterial technology

Nanomaterials are materials characterized by nanometric dimensions (1-100 nm) in one or more dimensions. Because of their different area, roughness, energetics, and electron distributions, the properties of nanomaterials are significantly different from those of bulk materials. Fascinating properties including physical, chemical, mechanical, magnetic, and optical ones make nanomaterials highly competitive in analytical chemistry [60]. The outstanding properties of these materials have been exploited to improve sensitivity, stability, selectivity of electrochemical (bio)sensors.

In Table 1, the electrochemical sensors for environmental analysis described in this review and based on electrodes configured with different nanomaterials have been reported.

3.1 Carbonaceous based nanomaterials

Carbon electrodes have been largely used since 1900 in research and industrial areas due to the excellent physical and chemical properties of carbon-based materials, including high conductivity, relative inertness, wide voltage range, and fast heterogeneous electron transfer. Carbon based nanomaterials including graphene, CNTs, and carbon black confer improved electrochemical performances with respect to bulk materials.

3.1.1 Graphene

Graphene is described by the International Union for Pure and Applied Chemistry (IUPAC) as “a single carbon layer of graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi-infinite size". The first efforts on graphene production dates back to 1859 [61]; however, this nanomaterial has only recently attracted enormous attention. In 2010, Geim and Novoselov received the Nobel Prize in Physics thanks to their article published in 2004 [62] reporting the remarkable observation of the electric field effect in thick monocrystalline graphitic film. In particular, this film remains metallic, continuous, and of high quality down to a few atomic layers. Graphene has been extensively applied in the last years in several sectors including electronics, nano-medicine, and electroanalysis as well. In the period analysed in this review, from 2010 to 2015, a huge number of (bio)sensors have been developed using graphene and applied for environmental monitoring.

Several graphene based sensors have been reported for the detection of heavy metal ions including Pb^{2+} and Cd^{2+}. One of the first papers was reported by Bank's group, where in the introduction they stated “Given the widespread exploration of graphene in many electrochemical areas, the use of graphene for target heavy metal ions is surprisingly limited” [63]. This group has found that the sensor modified with graphene has less sensitivity for Cd^{2+} detection with respect to bare electrode.

A deeply investigation was carried out, analysing the nucleation of the target metal via chronoamperometry and using a deposition potential of -1.3 V (vs. SCE) for 120 s. A lower charge of -0.78 mC was observed in the case of bare electrode if compared to the graphene modified electrode (-1.61 mC). The authors attributed this behaviour to the presence of surfactants like sodium cholate in PureSheets NanoIntegris (Illinois, USA) graphene fabrication, the one employed to modify the working electrode surface.

After 2011, many sensors for heavy metal ions have been developed with graphene using different routes, including bismuth modified sensors. For instance, Sahoo et al. [64] fabricated a highly performing sensor for Pb^{2+}, Cd^{2+}, Zn^{2+}, and Cu^{2+} by using a carbon paste electrode modified with a drop cast dispersion of reduced graphene oxide and bismuth. The authors highlighted that graphene oxide was produced by Hummers method avoiding the use of any surfactant. The modified electrode was able to detect simultaneously only Pb^{2+} and Cd^{2+} with a deposition potential of -1.05 V vs SCE. In the case of Zn^{2+} detection, a deposition potential of -1.25 V vs SCE was selected while Cu^{2+} detection was provided using an applied potential of -0.6 V vs SCE, achieving LOD equal to 2.8, 0.55, 17, and 26 µg L^{-1} for Cd^{2+}, Pb^{2+}, Zn^{2+}, and Cu^{2+}, respectively. Ground and lake water samples were analysed, detecting Cd^{2+}, Pb^{2+}, Zn^{2+} and Cu^{2+} concentrations of 1500, 3.3, 27 and 23 µg L^{-1}, respectively in West Bengal, and concentrations of 1600, 1.1, 12 and 26 µg L^{-1} were found respectively for Cd^{2+}, Pb^{2+}, Zn^{2+} and Cu^{2+} in Powai lake (Mumbai).

To enhance the sensitivity, graphene and bismuth were coupled with thiolated compounds. Li et al. [65] used glassy carbon electrode modified with a graphene oxide-thionine nanocomposite, 2-mercaptoethanesulfonate, Nafion and in situ Bi. Indeed, the presence of 2-mercaptoethanesulfonate was able to increase the sensitivity thanks to the thiolation reaction, resulting in a low detection limit equal to 0.1 and 0.05 µg L^{-1} for Cd^{2+} and Pb^{2+}, respectively. To assess the applicability of this sensor, the simultaneous determination of Cd^{2+} and Pb^{2+} in spring water from Yuelu mountain and water from Xiangjiang river (China) was carried out. The samples, prior the analysis, were filtered with a 0.22 µm membrane (Millipore), and afterwards acetate buffer (pH 4.5) containing Bi^{3+} was

added taking into account a dilution factor of 2.5. The accuracy was evaluated spiking the sample with 10 µg L^{-1} of Cd^{2+} and Pb^{2+}, obtaining satisfactory recovery values.

Exploiting the same principle of the thiolation reaction, Muralikrishna et al. [66] reported the use of graphene and another thiol compound namely L-cysteine. In particular, the graphene oxide was functionalised with L-cysteine at the edges and basal planes of the carbon layers with the reduction of graphene oxide and further functionalization with L-cysteine through amidation (between COOH of graphene oxide and NH_2 of L-cysteine) and nucleophilic substitution (between epoxide of graphene oxide and NH_2 of L-cysteine) in a single step. This novel sensor hold simultaneous electrochemical quantification of $Cd^{2+,}$ Pb^{2+}, Cu^{2+}, and Hg^{2+} with detection limits of 0.366, 0.416, 0.261, and 1.113 µg L^{-1} respectively. Various environmental samples including industrial effluent, pond water, and lake water were analysed and the results obtained were in agreement with atomic absorption spectroscopy data.

Besides these thiol compounds, many nanomaterials have been used in combination with graphene exploiting its high surface for loading of large amounts of nanomaterials and its high conductivity to provide smart electrochemical performances. For example, graphene, gold nanoparticles, and chitosan have been used to modify glassy carbon electrodes for Pb^{2+} detection in water samples [67]; a graphene and titanium dioxide nanoparticle based electrode was reported for the simultaneous determination of catechol and hydroquinone in lake water [68]; MWCNTs functionalized with carboxyl groups, together with graphene oxide were used to develop a carbon paste electrode for determination of tetracycline in river water [69]; reduced graphene oxide and MWCNTs were employed to modify a glassy carbon electrode for simultaneous determination of catechol, hydroquinone, p-cresol, and nitrite in river water [70]; a nanocomposite with three-dimensional Pd nanoparticles on the graphene surface was used for chlorophenol detection in wastewater [71]. In the latter example, the nanocomposite was attained by a novel sonoelectrochemical process, a niche route to produce Pd nanoparticles/graphene nanocomposites. In details, Pd complex ions firstly diffused towards the surface of the sonoelectrode, then, Pd

complex ions were electrochemically reduced to Pd nanoparticles. Later, when primary Pd particles reached a certain value, they spontaneously aggregated into larger Pd clusters with in some case in 3D spherical Pd nanoparticles on graphene sheet. This nanocomposite based on graphene, Pd nanoparticles and ionic liquid was characterized by a large electrochemical active surface with an excellent electrocatalytic activity allowing the detection of 2-chlorophenol at µM level with very high reproducibility (RSD equal to 0.78%) and accuracy when tested in river water (recoveries were in the range of 100.4–103.2%).

Alternative compounds have been also used in the development of sensors based on graphene. For example, Bagheri et al. [72] exploited graphene in combination with 1-n-octylpyridinum hexafluorophosphate and [2,4-$Cl_2C_6H_3C(O)CHPPh_3$] as ligand for the sensitive detection of Tl^+, Pb^{2+}, and Hg^{2+} in river and soil samples; Chen et al. [73] reported a modified glassy carbon electrode with by electropolymerized Poly(crystal violet) for Pb^{2+} and Cd^{2+} in river and lake water samples; Wang et al. [74] have developed a stannum film/poly(p-aminobenzene sulfonic acid)/graphene composite to modify glassy carbon electrodes and measure Cd^{2+} in industrial wastewater, lake, and farmland irrigation waters; Xu et al. [75] have designed a poly(malachite green)/graphene nanosheets-nafion nanocomposite to measure methyl parathion in river water; Lin et al. [76] realised electrodes by electro-polymerization of 7-[(2,4-dihydroxy-5-carboxybenzene)azo]-8-hydroxyquinoline-5-sulfonic acid at a graphene-nafion modified glassy carbon electrode for quantification of 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline in sewage samples; Tehrani et al. [77] used glassy carbon electrode modified with a composite film of graphene nanosheet and poly(4–vinylpyridine) for catechol and hydroquinone in lake water; Meng et al. [78] designed an ionic liquid-functionalized graphene nanosheet modified electrode for nonylphenol in river water sample; Moraes et al. [79] designed an electrode based on reduced graphene oxide and a metal porphyrin to quantify 17β-estradiol in river water sample.

Among the above-mentioned compounds, the use of β-cyclodextrin entailed the supra-molecular chemistry to improve the analytical performances. Lv et al. [80] reported a glassy carbon electrode

modified with hydroxypropyl-β-cyclodextrin-reduced graphene oxide hybrid nanosheets, Nafion, and Bi film for the simultaneous quantification of Cd^{2+} and Pb^{2+}. Under the optimal conditions, the limit of detection were estimated to be 9.42×10^{-11} M for Pb^{2+} and 6.73×10^{-11} M for Cd^{2+}, respectively. These low detection limits achieved were attributed to i) the host-guest recognition with the enrichment properties, ii) the large 2-D electrical conductivity and large-surface-area properties of reduced graphene oxide, iii) the ion-exchange property of Nafion, and iv) the ability of Bi to form alloys with Cd^{2+} and Pb^{2+}. The supramolecular recognition, as well as the enrichment capability properties, was exploited also in the case of organic pollutant detection.

Wei et al. [81] used β-cyclodextrin to functionalise graphene modified carbon paste electrode and to detect 2-chlorophenol and 3-chlorophenol. This sensor has the capability to simultaneous quantify 2-chlorophenol and 3-chlorophenol thanks to well separated oxidation peaks by differential pulse voltammetric analysis with LODs of 0.2 and 0.09 μM, respectively. To measure these analytes in river water, the sample only required the adjustment of the pH before the measurement allowing satisfactory recoveries of 98.4-103.6%. Wu et al. [82] developed highly sensitive sensor for methyl parathion detection using electrochemical reduced β-cyclodextrin dispersed graphene. This nanocomposite has demonstrated the capability to pre-concentrate methyl parathion due to its sorbent property via strong π–π interaction. The limit of detection achieved was 0.05 μg L^{-1}, which is more than 10 times lower than those obtained from other sorbent based sensors. Recoveries values from 96.0% to 111 % were found in filtered sea water samples.

A competitive host-guest interaction between β-cyclodextrin/poly(N-acetylaniline)/electrogenerated-graphene film and probe (rhodamine B) or target (1-aminopyrene) has been described by Zhu et al. [83]. The authors reported that in the absence of the target, rhodamine B was able to enter into the cavity of β-cyclodextrin displaying the electrochemical response of rhodamine B, while in the presence of 1-aminopyrene a competitive association to β-cyclodextrin occurred and the rhodamine B molecules were displaced with the consequent decrease of oxidation peak. This format allowed the detection of 1-aminopyrene at a very low concentration

(3.6 nM). Moreover, the suitability of this sensor was tested in real-water samples collected from a local river (Xiangjiang River, China), showing recovery value of 95-110% in agreement with high performance liquid chromatography data.

The use of graphene was described not only to enhance the electrochemical performances of sensors, but also to immobilise biological recognition elements improving their stability as well as their activity. For instance, an electrochemical biosensor to detect methyl parathion and carbofuran pesticides was reported by Zhou et al. [84] immobilising acetylcholinesterase on glassy carbon electrodes modified with carboxylic graphene, SnO_2 nanoparticles, and Nafion. This nanocomposite was characterised by an excellent conductivity, catalysis, and biocompatibility offering an extremely hydrophilic surface for acetylcholinesterase immobilisation. The biosensor exhibited high sensitivity towards methyl parathion and carbofuran with detection limit of 5×10^{-14} M and 5×10^{-13} M, respectively. The suitability of this biosensor to detect pesticide in lake water samples was also successfully demonstrated. The same authors have also used similar biosensors where SnO_2 nanoparticles were substituted by nickel [85] or silver [86] nanoparticles, showing low detection limits as well as very good recovery in real samples (lake water).

Another example of acetylcholinesterase immobilised on graphene for pesticide detection was reported by Wu et al. [87]. The biosensor was fabricated with electrochemically reduced graphene oxide and Nafion hybrid nanocomposite modified electrode. This nanocomposite showed conductive and three-dimensional interpenetrating network allowing for the detection of enzymatic product (thiocholine) at low applied potential (+ 50 mV vs SCE). The proposed electrochemical biosensor was able to detect dichlorvos with detection limit of 2.0 ng mL^{-1}. Recovery tests were also performed in river waters sampled from, Dalian Lingshui River with values from 92 % to 114 %.

Together with acetylcholinesterase, also tyrosinase enzyme immobilised onto the graphene modified working electrode surface was used as biocomponent. For example, Liu et al. [88] modified a glassy carbon electrode surface by drop-casting a dispersion of TiO_2 nanotubes grown

on graphene nanoplatelets, Nafion, and tyrosinase. This nanocomposite furnished a suitable microenvironment for tyrosinase to retain its enzymatic activity and facilitated the electron transfer kinetic. Indeed, this biosensor was able to detect catechol with a detection limit of 0.055 µM in standard solutions, and to accurately quantify 5, 10 and 20 µM in river waters.

Antibodies have been also used for hazardous chemical monitoring employing graphene as smart support for their immobilisation. For instance, Ruivi et al. [89] reported graphene oxide combined with gold nanoparticles, 2,5-di-(2-thienyl)-1-pyrrole-1-(p-benzoicacid) polymer, and ionic liquids to immobilise microcystin-LR antibody on glassy carbon to detect microcystin-LR in lake, river, and ground water (Figure 2A). Very low detection limit was attained (3.7×10^{-17} M) thanks to the enhancement of electron transfer of graphene-gold nanoparticles and the favourable microenvironment of ionic liquid for antibody.

3.1.2 Carbon nanotubes

Since their discovery in 1991 [90], carbon nanotubes (CNTs) have encountered remarkable interest in chemistry, physics, and material science due to their 1-D structure and unique properties. These tubular structures, composed by sp^2 carbon units, can exist principally as SWCNTs and MWCNTs. Thanks to their fascinating electronic, thermal, and adsorption properties, electronalysis takes advantage of CNTs to improve the performance of the analytical methods towards the detection of different hazardous chemicals.

In 1991, Nature published a letter of S. Iijima reporting the synthesis of nanometre-size and needle-like tubes of carbon namely helical microtubules of graphitic carbon, that now we called CNTs [90]. After this article, many research articles have been published entailing CNTs for several applications such as microelectronic circuitry, biological systems, and sensing devices. In the years comprised between 1991 and 2010, CNTs have played a prominent role among carbonaceous nanomaterials for developing electrochemical (bio)sensors, while in the period analysed in this

review their leading position was tarnished by graphene. However, the numerous properties of CNTs, including the electrocatalytic properties as well as the high surface area to immobilise nanomaterials and/or biocomponents, have been largely exploited for the design of electrochemical (bio)sensors applied in the environmental field. The electrochemical properties of CNTs were deeply investigated by Compton's and Pumera's groups. The electrocatalytic properties in terms of catalytic activity, electron transfer, and chemical reactivity seem relay on their surface defect sites, and in particular edge-plane-like defect sites, as reported in 2005 on Chemical Communication by Compton's group [91]. The relevant effect of the impurity for sensitive detection of phenolic compounds was explained by Prof. Pumera's group [92]. The authors stated "We unambiguously demonstrate that the reported stability and sensitivity exhibited by CNTs is not actually 'inherent' to CNT materials but is instead caused by the nanographite impurities contained within them" demonstrating the questionable properties in electrochemical chemistry field of CNTs. Regarding this finding, it is extremely important to characterise carbon nanomaterials to be employed in the sensor fabrication by means of key techniques such as Raman Spectroscopy, X-ray Photoelectron Spectroscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy. Indeed, an inclusive knowledge on nanomaterials can give an exact correlation between the electrochemical properties and the structural and functional characteristics of nanomaterials [94]. For instance, X-ray Diffraction, Transmission Electron Microscopy, and High-Resolution Transmission Electron Microscopic techniques have been used to characterise MWCNTs decorated with gold nanoparticles for paraoxon detection at nanomolar level [94] or ZnO/CNTs nanocomposite for simultaneous determination of hydrazine and phenol in river water and wastewater samples [95].

CNTs have been employed for sensor fabrication principally coupled with other nanomaterials, compounds, or/and biocomponents. Dong et al. [96] developed a glassy carbon electrode modified with nanocomposite constituted of MWCNTs–CeO_2–gold nanoparticles for methyl parathion detection with detection limit of 3.02×10^{-11} M. A high sensitivity was achieved since the nanocomposite was capable of the solid-phase extraction due to exceptional adsorption properties of

MWCNTs. In addition, the use of CeO_2 and gold nanoparticles entailed the high surface area and the special catalytic activity with sensitivity improvement for methyl parathion detection in river and soil samples.

An interesting hybrid nanocomposite constituted of one-dimensional MWCNTs and two-dimensional graphene oxide sheets was reported by Huang et al. [97] (Figure 2B). This nanocomposite was characterised by an excellent conductivity and a good water-solubility, and it was used to modify glassy carbon electrodes for the detection of Pb^{2+} and Cd^{2+} with a detection limit of 0.2 µg L^{-1} and 0.1 µg L^{-1}, respectively. The authors highlighted that the effective combination of two carbon nanostructures exploits the respective advantages and overcoming respective deficiencies, since the hydrophilic graphene oxide sheet components may load CNTs through π-π overcoming the solubility problem while the presence of CNTs components suppresses the aggregation between graphene oxide nanosheets. This sensor was able to detect Pb^{2+} and Cd^{2+} in real samples from electroplating effluent requiring only filtration with a 0.22 µm membrane (Millipore filter) as sample treatment followed by the addition of acetate buffer (pH 4.5) containing 500 mg L^{-1} Bi^{3+}.

The use of ionic liquids, as reported also in the case of graphene, has enlarged the analytical properties of the nanomodified electrodes exploiting their high conductivity and sensitivity, fast electron transfer, and good antifouling ability. For instance, Afkami et al. [98] developed a carbon paste electrode using MWCNTs and octylpyridinum hexafluorophosphate for Cd^{2+} measurement in industrial waste water and Persian gulf water samples; Khani et al. [99] fabricated an ion-selective electrode with 1-n-butyl-3-methylimidazolium tetrafluoroborate and MWCNTs for the determination of Hg^{2+} in sea and river water.

Besides ionic liquids, several polymers have been used in combination with CNTs. For instance, chitosan was employed in CNTs paste electrode fabrication for the determination of Cd^{2+} and Hg^{2+} at nanomolar level. The practical use of this sensor was demonstrated in industrial wastewater samples as well as in sediments for the Cd^{2+} analysis [100]. Poly(acrylamide) was also employed to

design a MWCNTs–poly(acrylamide) nanocomposite to modify a glassy carbon electrode for detecting methyl parathion. This sensor accomplished the pesticide quantification with a detection limit of 2.0×10^{-9} M in river water [101]. Poly-sodium 4-styrenesulfonate with CNTs and bismuth were used as platform for Pb^{2+} and Cd^{2+}measurement, with detection limits of 0.04 µg L^{-1} for Pb^{2+} and 0.02 µg L^{-1} for Cd^{2+} [102]. The concrete application of this sensor was verified in lake water samples with satisfactory results, demonstrating that the improved analytical performances were ascribed to the small size, the larger surface area, and the high adsorptive ability of this composite, in combination with the special electrochemical properties of CNTs.

The special structural and functional features of CNTs have been also exploited for biocomponent immobilisation, as reported by Vicentini et al. [103] (Figure 2C). The authors reported the immobilisation of tyrosinase on CNTs using their carboxylic moieties. In detail, tyrosinase was covalently immobilised onto CNTs by means of (1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide) and N-hydroxysuccinimide, and this biosensor was successfully applied for catechol detection in lake water demonstrating the ability of CNTs as smart nanomaterials for the effective biocomponent loading together with the improvement of the electrochemical biosensor performances.

3.1.3 Carbon black

Carbon black (CB) is a form of amorphous carbon that has an extremely high surface area to volume ratio, and it has been one of the first nanomaterials to find a common use. The most common use [70%] of CB is as a pigment and a reinforcing phase in automobile tires. Few applications are reported in literature until 2010 using CB as sensing element for analyte detection in solution [104-107]. After 2010, several works have demonstrated the interesting properties of CB as nanomaterial to improve the electrochemical behaviour of electrodes. In particular, our group described the fascinating electrochemical properties of CB in the ink/paste as well as in modifying electrodes by drop casting for the determination of several analytes including catechol, hydrogen

peroxide, NADH, and thiocholine [108-111]. Our results have been also corroborated by other groups, like Compton's group [112] that reported the gain of using CB over the more specialized MWCNTs. Pumera's group [113] has also proved that CB is more convenient than the thermally reduced graphene oxide, and Fatibello-Filho's group [114] as well as Evtugyn's group [115] successfully used CB modified electrode for the detection of different analytes.

The electrocatalytic properties of CB were exploited in environmental analysis for mercury ions as well as pesticide detection. In the former case, Hg^{2+} was quantified measuring the decrease of the thiocholine signal due to the formation of the non-electroactive complex between thiocholine and Hg^{2+}. This sensor is capable to detect mercury ions with a detection limit of 1 µg L^{-1} [116]. In the latter case, the butyrylcolinesterase enzyme was immobilised on the working electrode surface, previously modified with CB, by means of glutaraldehyde, albumin bovine serum, and Nafion [117]. The pesticide paraoxon was detected exploiting the inhibition capacity towards BChE with a detection limit of 5 µg L^{-1}. This biosensor was successfully applied for paraoxon detection in spiked wastewater samples with high recovery values.

CB was also employed for phosphate detection by Talarico et al. [118] in amperometric mode via electrochemical reduction of molybdophosphate complex at CB modified electrodes. The presence of CB allowed the quantification of molybdophosphate complexes at a low applied potential without fouling problem. Under optimised conditions, a linear range of 0.5 - 100 µM was observed with a detection limit of 0.1 µM. The suitability for phosphate detection in river and aquarium water samples was successfully demonstrated, yielding recovery values in accordance with the spectrophotometric reference method.

The suitability of CB in electroanalysis was also explored preparing hybrid nanocomposites with gold nanoparticles for As(III) and Hg(II) detection, respectively in water and soil samples [58, 59].

The high surface of CB was exploited to load the electrochemical mediator cobalt phthalocyanine by a non-covalent physisorption obtaining a stable dispersion, useful for fabrication of reproducible sensors by drop casting. The resulting CB/cobalt phthalocyanine-modified SPE was used as

platform to immobilise butyrylcholinesterase and to detect the organophosphorus pesticide paraoxon down to 18 nM [119]. The suitability of this biosensor was tested in a waste water sample obtaining satisfactory recovery values, thus demonstrating its capability in such complex matrix.

These different applications have demonstrated the applicability of CB as nanomaterial in the design of sensitive sensors for pollutant detection. The advantage of CB in comparison with the more famous graphene and CNTs relies on its huge electrochemical performances coupled with the cost-effectiveness (around 1 € for 1 Kg), as well as its simple and sustainable use without the need of any treatment.

3.1.4 Other Carbonaceous nanomaterials

Beside graphene, CNTs, carbon black, and other carbonaceous nanomaterials have been investigated for the developing of (bio)sensors for pollutant monitoring. Electrospun carbon nanofiber is an interesting material belonging to carbon based nanomaterials. This nanomaterial has similar electronic properties of CNTs, it is characterised by higher purity (since its synthesis does not require any catalyst) and it can be used directly without further oxidative pre-treatment. In addition, the presence of more edge sites on the outer wall may lead to an improved electron transfer [120]. A crucial example of electrospun carbon nanofiber-modified carbon paste electrodes for the simultaneous determination of catechol and hydroquinone using differential pulse voltammetry was reported by Guo et al. [121]. This sensor exhibited higher electrocatalytic activity toward the oxidation of catechol and hydroquinone, allowing their detection down to 0.2 and 0.4 µM, respectively. Finally, it was successfully applied for the simultaneous determination of catechol and hydroquinone in lake water samples.

Among carbonaceous nanomaterials, nanospheres are a long-standing material. However, taking advantage of the recent amazing powerful of nanotechnology, nanocarbon spheres can be nowadays

custom-made, tailoring control of particle size, surface area, pore size, chemical composition, and dispersity as well [122].

For example, Wei et al. [123] used carbonaceous nanospheres combined with polypyrrole for SPE modification to detect Hg^{2+} and Pb^{2+} at ultra-low concentration. The method was focused on Hg^{2+} and Pb^{2+} adsorption on carbonaceous nanospheres/polypyrrole allowing for their detection at levels as low as 0.0041 nM and 0.0214 nM, respectively. In addition, the practicality of this sensor was demonstrated measuring Pb^{2+} and Hg^{2+} in ground water from Dongpu Reservoir in Hefei City, Anhui province, China, without requiring sample treatments.

Carbon dots are rather novel fluorescent nanoparticles which are incidentally discovered during the electrophoretic purification of SWCNTs derived from arc-discharge soot. These nanomaterials might display comparable electrocatalytic activity with respect to graphene; however, their application in electrochemical sensors still remains at an early stage. A recent paper was reported by Yu et al. [124] in which a sensitive electrochemical detection 2,4-dichlorophenol was achieved using sensor modified with a nanocomposite constituted of carbon dots, hexadecyltrimethyl ammonium bromide, and chitosan. Differential pulse voltammetry was selected as a technique for quantifying 2,4-dichlorophenol down to 0.01 μM. This sensor displayed good accuracy and selectivity in the detection of 2,4-dichlorophenol in lake water samples.

3.2 Metallic nanoparticles based nanomaterials

Metallic nanoparticles have been widely employed in (bio)sensor field for their valuable electrochemical properties, the high affinity towards heavy metal ions, the capability to create a favourable environment for the biocomponent, and the suitability as labels in immunoassays as well.

The appreciated electrochemical properties of metallic nanoparticles have been for instance exploited in combination with liquid ionic and graphene. Hu et al. [125] reported a gold

nanoparticle and graphene composite film co-electrodeposited on a carbon ionic liquid electrode for hydroquinone detection at µM level in synthetic wastewater samples with satisfactory recovery values.

Gold nanoparticles have been also coupled with polymers as in the case of poly(o-phenylenediamine-aniline film) used to fabricate gold nanoparticle-modified glassy carbon electrode for nitroaromatic compound detection [126]. The authors ascribed the low detection limits achieved (2.1 mg L^{-1} for 2,4,6-trinitrotoluene, 1.28 mg L^{-1} for 2,4-dinitrotoluene, and 3.8 mg L^{-1} for tetryl) to π–π and charge-transfer interactions between the electron-deficient nitroaromatic compounds and σ-/π-donor amine/aniline groups linked to gold nanoparticles, which provided an increased binding and pre-concentration on the modified electrode. A proficient data treatment by using a deconvolution approach of peak intensity allowed for selective detection.

Gold nanoparticles have been also exploited for heavy metal ion detection by means of anodic stripping analysis, thanks to their high affinity towards these metals. For example, zinc and cadmium ions were measured by using a gold electrode modified with gold nanoparticles, cysteine, and dipicolinic acid achieving detection limits of 0.008 µM and 0.015 µM, respectively [127]. This sensor was applied in lake, river, and spring water samples without any treatment, but with only pH adjustment before the measurement. As(III) was detected by means of an electrode modified with Nafion and gold nanoparticles with a LOD as low as 0.047 µg L^{-1} (0.63 nM) [128]. In addition, the authors reported the use of EDTA as chelating agent to enhance the sensitivity of the sensor and overcome the interference of Cu^{2+} and Hg^{2+}, considered the major interferences in the As(III) detection. This sensor was suitably applied for As(III) analysis in lake water samples with a recovery value of 102.0%.

Mercury ions detection has been accomplished by a simple, highly sensitive, and selective carbon nanocomposite electrode, designed by incorporation of thiolated amino acids capped gold nanoparticles into the carbon ionic liquid electrode. This sensor extraordinarily improved sensitivity and selectivity thanks to the presence of thiolated aminoacids allowing for LOD of 2.3 nM. The

proposed nanocomposite electrode exhibited good applicability for monitoring Hg^{2+} in waste water [129].

Along with gold nanoparticles, silver nanoparticles have been also employed in sensor fabrication for heavy metal ion detection. For example, Prakash et al. [130] configured a silver nanoparticle built-in chitosan-modified glassy carbon electrode with the capability to detect As(III) with 1.20 $\mu g\, L^{-1}$ (16.2 nM) as LOD. The low LOD was achieved due to the unique three-dimensional networks and strong adsorption ability of the nanoparticles. The sensor was applied for As(III) quantification in different samples obtained from ground water of Ranaghat, Nadia district (West Bengal, India), and Bhavnagar (Gujarat, India), being India a country affected by As contamination. Indeed, this sensor revealed 12.3 $\mu g\, L^{-1}$ of As(III) in samples of Ranaghat, in agreement with the data obtained with Metrohm 797 VA voltammetric metal analyser which requires a rotating gold electrode as working electrode.

To fabricate the metallic nanoparticle based sensor, the modification by drop casting and the electrochemical reduction of metal salts are the most used routes. However, a novel method using laser ablation in liquid for the fabrication of gold nanoparticles was recently proposed. As described by Xu et al. [131] gold nanoparticles were embedded in the surface of a glassy carbon electrode using electrophoretic deposition and this modified sensor was devised to simultaneously detect Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+} with LOD as low as 3×10^{-7} M.

The nature of nanoparticle production is also a crucial step to confer different features to nanoparticles in terms of different dimensions and consequently different sensitivity, as reported by Hezard et al. [132]. The authors studied three different electrochemical techniques namely cyclic voltammetry, chronoamperometry, and potentiostatic double-pulse to electro-deposit gold nanoparticles on electrodes. Gold nanoparticles obtained by chronoamperometry resulted in the smallest particle size (ca. 17 nm in diameter) and the highest particle density (332 particles μm^{-2}) reaching a low detection limit (0.40 nM) for mercury ion measurement.

Metallic nanoparticles have been also employed to create a favourable environment for the biocomponent immobilization, allowing for improved storage stability. For instance, composite of sol-gel and polyvinylpyrrolidone stabilized gold nanoparticles were prepared and used as matrix for tyrosinase enzyme immobilisation to detect catechol with LOD of 3×10^{-7} M [133]. In detail, spin coating was used to have a homogenous coverage of the working electrode surface, providing a long term storage stability of 6 weeks, after that the decreased signals were ascribed to the enzyme inactivation during the time. The feasibility of this biosensor was evaluated in water samples with satisfactory recovery values. Another example was reported by Karim et al. [134] which immobilised tyrosinase on gold nanoparticles electrodeposited onto a disposable SPE for the detection of phenol at concentration of 47 μg L^{-1}, with a linear response up 15 mg L^{-1} in regional water samples from S. Korea. The authors demonstrated the long-term stability of the biosensor by repeatedly measuring the response at a fixed phenol concentration of 2 mg L^{-1} eight times a day, while the sensor was kept in the 0.1 M phosphate buffer (pH 7.0) all the time. Results indicated that the sensor was suitable for 3 days measurements, with a relative standard deviation of 11.1%.

The type of gold nanoparticles to provide a large surface area and good biocompatibility was demonstrated also by Fu et al. [135]. They reported the design of a label-free electrochemical immunosensor using gold nanoparticles/silicon template/methylene blue/chitosan nanocomposite-modified electrode for the detection of microcystin-LR. The amount of toxin was evaluated measuring the decrease of methylene blue response signal in differential pulse voltammetry, which is linear with the concentration of microcystin-LR, allowing for LOD of 0.1 ng/mL. This immunosensor was tested for the detection of microcystin-LR in real water samples collected from Dian Lake of Kunming city (China), displaying satisfactory agreement with data from a microcystin detection kit.

Metallic nanoparticles have been also utilised as tag to monitor the reaction between the biocomponent and the target analyte. Tang et al. [136] reported a label-free electrochemical sensor to monitor of Hg^{2+} exploiting the specific thymine-Hg^{2+}-thymine coordination. The presence of the

complex was monitored by the catalytic $HAuCl_4/NH_2OH$ formation of gold nanoparticles as signal reporter, detected by stripping voltammetry. This system was challenged for Hg^{2+} detection in spiked river water samples collected from MingJiang (FuJian, China) with recovery values ranging from 97.5 to 108.0%.

3.3 Other nanomaterials

Nano-silica was discovered by scientists at the Mobil Corporation in 1992 and after that, it was applied in several fields due to its large surface area coverage, biocompatibility, high ionic conductivity, and chemical and thermal stability [137]. Mesoporous silica nanoparticles were used to modify SPE for reliable measurements of Pb ions at $\mu g\, L^{-1}$ level by anodic stripping voltammetry in non-pretreated river water and groundwater [138]. Mesoporous silica nanoparticles were also used combined with bismuth film for the quantification of Pb^{2+} and Cd^{2+} with LODs of 0.2 $\mu g\, L^{-1}$ and 0.6 $\mu g\, L^{-1}$, respectively [139]. In this case, the fibril-like bismuth structures formed on silica nanoparticles with enhanced surface area showed improved sensor performances. This sensor was applied for the analysis of Pb^{2+} and Cd^{2+} in several lake water samples, obtaining data in agreement with reference values from inductively coupled plasma mass spectrometry method.

A nanocomposite based on carboxylic silica nanosheets, platinum nanoparticles, and Nafion was employed to modify glassy carbon for acetylcholinesterase biosensor fabrication [140]. This biosensor was tested using methyl parathion and carbaryl as organophosphorus and carbamic pesticides, obtaining LODs as low as 5.52×10^{-13} and 5.65×10^{-13} M, respectively. Finally, the suitability of this probe for pesticide detection in real sample was demonstrated using lake water.

Mesostructured silica nanoparticles functionalized with a 5-mercapto-1-methyltetrazole derivative were also reported in literature to prepare a chemically modified carbon paste electrode for Hg^{2+} detection [141]. The voltammetric responses displayed a detection limit of 0.023 µM with good

reproducibility. In addition, its applicability was demonstrated using spiked groundwater and river water without requiring any sample pre-treatment.

Other nanomaterials including hydroxyapatite and ZrO_2 nanoparticles were exploited to design (bio)sensors. Lu et al. [142] developed a tyrosinase biosensor based on hydroxyapatite nanoparticles-chitosan nanocomposite for the detection of phenolic compounds by monitoring the reduction signal of the biocatalytically produced quinone species at −0.2 V (vs. SCE). This biosensor showed a limit of detection down to 5 nM, and its suitability was successfully evaluated by the recovery of spiked phenolic real wastewater samples. Another example was reported by Parham et al. [143] which constructed a sensor for square wave voltammetric detection of methyl parathion using ZrO_2 nanoparticles. These nanoparticles were selected owing to their strong affinity toward the phosphate group of methyl parathion molecules, allowing a detection limit of 2 μg L^{-1}. Recovery tests in river water demonstrated the reliability of this sensor in real matrices.

A new kind of nanomaterial based on molybdenum-chalcogenide-halide nanowires in the form of $Mo_6S_{9x}I_x$ was employed to modify glassy carbon electrode for simultaneous detection of Cd^{2+}, Pb^{2+}, and Cu^{2+} by voltammetry [144]. Using this sensor and DPASV as technique, LODs were estimated to be 0.10 μg L^{-1} for Cd^{2+}, 0.45 μg L^{-1} for Pb^{2+}, and 0.20 μg L^{-1} for Cu^{2+}. LODs achieved were two orders of magnitude lower than those obtained at the unmodified electrodes, demonstrating the advanced properties of this nanomaterial even when applied in water samples.

An interesting multiple hybrid $CdSe_xTe_{1-x}/TiO_2$ nanotube structure was conceived by Kang et al. [145] to develop a label-free immunosensor for pentachlorophenol. In detail, $CdSe_xTe_{1-x}$ nanocrystals were photo-electrodeposited on inner and outer space of the TiO_2 nanotubes, to obtain high photoelectrical conversion efficiency in the visible region. Furthermore, TiO_2 was also used to immobilise pentachlorophenol antibodies exploiting their large surface area and good biocompatibility as well. The detection was based on the fact that the photocurrent is highly dependent on the TiO_2 surface properties, reason for that the specific interaction between target

analyte and antibodies gave a significative change in the photocurrent. This architecture enabled a LOD for pentachlorophenol of 1 pM with satisfactory accuracy also in river water samples.

4. Nanomotors

The terms "nanomotors" and/or “nanomachines” host many different nano- and micro-scale objects, including rods, rockets, Janus particles, engines, and pumps. Proteins like myosins, kinesins, and dyneins represent natural occurring chemically-powered motors [146]. They are capable to perform many physiological tasks, for example they are responsible for powering the movements of microtubules involved in vesicles and organelles transportation. These natural molecular motors need ATP as fuel to convert chemical energy into mechanical work. Inspired by nature, manmade nanomotors (i.e. wires, tubes, and Janus spheres) use a chemical fuel to get a movement.

Among diverse routes, these tiny objects can be mainly mass-fabricated by: i) membrane-template electrodeposition, and ii) physical vapour deposition. Membrane-template electrodeposition allows, for example, to mainly produce wires, tubes, and rockets, via cylindrical or conical pores of a membrane (i.e. alumina, polycarbonate) followed by the template dissolution. Thus, sequent deposition of noble metals and/or polymer segments endows asymmetric objects generating a directional force in the presence of fuel. The group of Prof. Wang fabricated a flexible Pt/Au/Ag/Ni nanowire propelled by hydrogen peroxide and magnetically driven [147]. The same group incorporated CNTs into the Pt end of a nanowire enhancing the electron transfer, and consequently the speed [148].

Physical vapour deposition represents another facile route to fabricate nano/micromotors, using miscellaneous supports that can be finely coated by the heating and evaporation of metals and metal oxides to obtain different shaped particles. As an example, Janus particles can be fabricated exploiting silica or polysterene spheres half-coated with differing materials, including Pt/Au [149], Ir/SiO_2 [150], TiO_2/Au/Mg [151]. The group of Prof. Fischer was the first to produce 30-nm sized

Janus particles made of PtNPs half-coated by gold, capable to catalyse the decomposition of hydrogen peroxide and move by self-electrophoresis [152].

Thanks to these fabrication strategies, many examples of these wondering objects have been reported in literature, finding several applications in different fields such as cargo loading, environmental remediation, and biomedical field (i.e. malignant cell destruction, drug delivery, and microsurgery) [153-159].

Recently, the utilization of these kinds of fully-autonomous objects is moving towards electroanalytical applications. In 2015, Cinti and colleagues [160] firstly coupled Janus microparticles to printed electrodes fabricating specific microengines composed by gold, nickel, and magnesium for the remediation/detection of organophosphorous pesticides in aqueous solutions. These microengines displayed brilliant remediation capability in hydrolysing paraoxon in a chloride-rich environment, producing a non-hazardous compound, p-nitrophenol, subsequently detected at the electrode surface by means of a simple cyclic voltammetric scan. In details, Janus microparticles, immobilised on printed electrodes by using a magnetic field, were able to produce OH^- due to oxidation in aqueous solution of Mg present on the microparticles. The resulting OH^- is thus able to subsequently hydrolyse paraoxon producing p-nitrophenol (Figure 3).

Recently, the same concept was re-adapted by the group of Prof. Escarpa for the remediation/detection of diphenyl phthalate in food and biological samples [161]. They developed a Mg/Au Janus micromotor for the degradation of diphenyl phthalate into phenol, thus determined by difference pulse voltammetry using screen-printed electrodes. This nanomotor was successfully applied to the direct analysis of diphenyl phthalate in real samples with recoveries of ~100%, showing advantages such as disposability, portability, and simultaneous multiple analysis.

5. Biomimetic design

Many efforts have been accomplished in the last years to meet the requirements of stability and sensitivity of biosensors through the development of new materials inspired by nature. To this regard, emerging and converging technologies like bioinformatics, genetic engineering, biomimetic design, and synthetic biology, have conferred the ability to design new synthetic molecules simulating key properties of natural ones but with custom-made function and structure. Indeed, novel synthetic cells can be projected for sensing application as well as new artificial molecules synthesised, including aptamers, peptidomimetics, and molecular imprinting polymers, with ad hoc designed features of sensitivity, selectivity, and robustness. Several synthetic entities have been further exploited for the development of electrochemical biosensors for hazardous chemicals, as widely reported in literature.

Aptamers have also gained momentum in the last showing enhanced advantages towards antibodies. Indeed, aptamers can be produced by accurate, reproducible, and cost-effective processes while antibodies are generated by animal immunization or cell clone technology. In addition, aptamers do not encounter the typical challenges to which antibodies are subjected, like pH and temperature sensitivity, short shelf life, and easily degradation [162]. In addition, antibodies, beside aptamers, are not feasibly produced against small size targets (e.g. metal ions) [163].

For these reasons, biosensors based on aptamers as biorecognition elements, coined aptasensors, are a valid alternative for environmental analysis where real sample matrices represent multifaceted analytical challenges. The principle based on electrochemical aptasensors relies on the significant conformational changes described by aptamers upon target binding, due to their high structural flexibility, conferring high sensitivity and selectivity to the detection. The property of aptamer conformational changes upon target binding makes them appropriate candidates also to design label-free formats, facilitating the detection of small size analytes. This aptasensor configuration determines target analytes when current or resistance changes arise, due to the recognition reaction

between aptamers and analytes. As an example, Fan et al. [164] designed a label-free aptasensor for the sensitive and selective quantification of acetamiprid by electrochemical impedance spectroscopy (Figure 4A). The authors reported the use of gold nanoparticles electrodeposited on the bare gold electrode surface by cycle voltammetry for aptamer immobilization to improve the sensitivity. Indeed, an increase of electron transfer resistance, in an acetamiprid concentration dependent manner, occurs upon the formation of the acetamiprid-aptamer complex on the gold nanoparticles-deposited electrode surface. Acetamiprid was quantified in a linear range from 5 to 600 nM with a LOD of 1 nM, without interferences from other pesticides similar to acetamiprid that may be present in the sample. In addition, a dissociation constant value of 23.41 nM for acetamiprid–aptamer complex further indicated its high selectivity. The applicability of the aptasensor was demonstrated also in real samples as wastewater with recovery values from 94.0 to 103.4%. Another crucial example of label-free electrochemical aptasensor is the one designed by Fei et al. [165]. The authors described an ultrasensitive label-free electrochemical impedimetric aptasensor for acetamiprid detection immobilising a selected aptamer on a gold nanoparticles decorated MWCNTs -reduced graphene oxide nanoribbon composites. This label-free sensor relied on the electron transfer resistance variation caused by the formation of acetamiprid–aptamer complex on the modified electrode surface, directly quantifying acetamiprid in the range 5×10^{-14} M - 1×10^{-5} M with a detection limit of 1.7×10^{-14} M. this sensor was also challenged in real water samples giving recovery values comprised between 96.0 % and 106.6 %.

Besides aptamers, DNA based sensors exploiting DNAzyme or DNA probe have been reported in literature for the detection of compounds of environmental interest. Zhou et al. [166] realised a label-free impedimetric sensor exploiting DNAzyme mesoporous carbon-gold nanoparticles for Pb^{2+} detection. Gold nanoparticles deposited on the modified electrode surface were employed as a platform for the immobilization of thiolated probe DNA, and hybridized with DNAzyme catalytic beacons. The DNAzyme was activated in the presence of Pb^{2+}, to cleave the substrate strand into 2 fragments, producing changes in the electrical properties of the film. Thus, when the charge transfer

resistance value for the $[Fe(CN)_6]^{3-/4-}$ redox indicator is analysed by electrochemical impedance spectroscopy, a strong decay after hybridization occurred, with a Pb^{2+} concentration range from 5×10^{-10} to 5×10^{-5} M, and a LOD of 2×10^{-10} M. This biosensor showed a promising potential for Pb^{2+} detection also in real samples (lake water from Taozi Lake and fresh river water from Xiangjiang River). To report an example, the concentration of total Pb^{2+} in the sample of river water was detected at a concentration of 17.35 nM in reasonable agreement with the concentration measured by inductively coupled plasma mass spectrometry (18.21 nM).

Molecular imprinting polymers (MIPs) have been also largely described in literature as a synthetic material that contains an artificial recognition site able to mimic a natural molecule in binding a highly specific target analyte. They can be prepared by the polymerization of functional monomers around a template molecule, which represents the target, by means of covalent or non-covalent bonds. Upon polymerization, the target molecule is removed and a specific recognition sites results to be complementary to the target in size, shape and position of the functional groups. The resultant molecules can be exploited in binding assays or sensors, because of their special features in terms of high affinity, selectivity, stability, simplicity of preparation, and ease of adaptation to different configuration. Furthermore, MIPs display high thermal, chemical, and mechanical tolerance, resistance to enzymatic degradation, heat, and low pH, as well as good performance in both aqueous and organic solvents [167]. For these reasons, a significant number of MIP based sensors have been realised employing conductometry, impedance, potentiometry, amperometry, and voltammetry, to reveal a wide range of chemical species, such as phenols [168], 2,4-dinitrophenol [169], herbicides [170], and bisphenol A [171]. Phthalates have been also monitored in environmental samples by means of molecular imprinting polymers sensors. As an example, dibutyl phthalate was detected by using an ad hoc synthesised composite of magnetic graphene oxide@gold nanoparticles-molecular imprinted polymers [172] (Figure 4B). Under optimal experimental conditions, selective detection of dibutyl phthalate in a linear range of 2.5×10^{-9} - 5.0×10^{-6} M was achieved, as well as an

excellent repeatability, with RSD of about 2.50 % for 30 repeated analyses of 2.0×10^{-6} M dibutyl phthalate.

Synthetic cells have also attracted widespread attention for the development of custom-made biosensors for the detection of hazardous chemicals for environmental analysis. For example, Cortés-Salazar et al. [173] described a whole-cell based sensor for arsenite detection coupling biological engineering and electrochemical techniques (Figure 4C). Indeed, the authors, exploiting the natural capability of Escherichia coli to selectively recognise arsenite, designing a genetic variant equipped with a genetic circuit in which the synthesis of beta-galactosidase was under control of the arsenite-depressable arsR-promoter. The E. coli reporter strain was filled in a microchip containing 16 independent electrochemical cells (where each cell consisted of a working electrode (Au) and a reference/counter electrode (Ag)), employed to analyse tap and groundwater samples, obtaining a very good limit of detection of 0.8 $\mu g\ L^{-1}$. Additionally, a very good linear response in the ranges of concentration tested (0.94 $\mu g\ L^{-1}$ to 3.75 $\mu g\ L^{-1}$, R^2=0.9975, and 3.75 $\mu g\ L^{-1}$ to 30 $\mu g\ L^{-1}$, R^2=0.9991) was obtained, complying with the tolerable arsenic concentration limits in drinking water regulated by the World Health Organization (10 $\mu g\ L^{-1}$). This biosensor demonstrated how synthetic biology coupled with electrochemistry was able to provide a valid alternative for the quantification of As (III) in water in accordance with the results obtained by atomic absorption spectroscopy.

6. Microfluidics and lab on a chip

The huge advantage resulting from the integration of multidisciplinary technologies including microfluidics, microengineering, and nanotechnology is widely demonstrated by the novel design of clever sensing platforms capable of high throughput analysis of complex environmental matrices [174]. Microfluidics allows to project platforms consisting of a network of channels and wells embedded into glassy or polymer chips, enabling sample handling, mixing, dilution, electrophoresis

and chromatographic separation, staining and detection. In addition, microfluidics can be considered an attractive approach in conjunction with electrochemistry, being both compliant for easily miniaturisation with minimal loss of performance at reduced scale. Without a doubt, a growing number of electrochemical lab-on-a-chip demonstrated the helpfulness of microfluidics for the detection of several chemicals of environmental interest.

Among these chemicals, heavy metal ion detection by means of microfluidic chips has been extensively described in literature. A crucial example is furnished by the polymer lab chip sensor reported by Jang et al. [175] for the measurement of pH and nitrates in groundwater as well as for the determination of Cd^{2+}. In details, a self-assembly nanobeads-packed hetero column on a polymer lab chip was deployed for the potentiometric analysis of pH and nitrate. While, Cd^{2+} quantification in aqueous samples was delivered integrating the polymer lab chip with electrochemical sensors based on square-wave anodic stripping voltammetry, obtaining a sensitivity of 24 nA μg^{-1} L and a LOD of 9.3 $\mu g\ L^{-1}$. This sensor showed how microfabrication technology can lead to the design of portable platform, through the construction of a microfluidic chip and a microsensor chip with planar microelectrodes then bonded by the fusion bonding method.

Jung et al. [176] reported a similar sensor for Pb^{2+} detection by square-wave anodic stripping voltammetry. The authors realised a reusable polymer lab chip sensor for lead continuous and on-site monitoring based on a microfabricated silver working electrode, an integrated silver counter and quasi-reference electrode, coupled with a system of microfluidic channels. Pb^{2+} was detected in a concentration range of 1-1000 $\mu g\ L^{-1}$ with a detection limit of 0.55 $\mu g\ L^{-1}$, with high repeatability and linearity of the sensor in a large dynamic range, demonstrating its potential for repeated on-site measurements in soil pore water or groundwater.

Cr(VI) determination was provided by using a lab-on-a-chip integrated electrochemical detector combined with custom USB electrochemical system, reported by Li et al. [177]. The authors described the great advantages of such system in terms of high sensitivity (LOD = 0.9 µM) and good reproducibility, portability, ease of use, low analyte consumption, low cost, fast response time,

demonstrating its high potential for high-throughput and in-field environmental monitoring in a wide linear range from 2 to 200 μM. In addition, satisfactory results were achieved in tap and sewage water, with recoveries from 96.42 to 102.15% (RSDs = 0.45-2.54%), demonstrating the high suitability of the proposed sensors also in real samples (i.e. industrial and domestic sewage samples).

Hg^{2+} detection was achieved using an on-chip integrated two-metal electrode system (Ag reference electrode, Au working/counter electrodes) coupled with a microfluidic channel, fabricated with two-step photolithography by Chen et al. [178]. This on-chip integrated electrochemical detector exhibited various benefits including the easiness to use, low analyte consumption, fast sensing time, and suitability for in situ analyses with high sensitivity and reproducibility (RSD 3% and 7%, for 25 μg L^{-1} and 250 μg L^{-1} Hg^{2+}, respectively).

Pesticide analysis has been also widely accomplished exploiting microfabricated chips. Wang et al. [179] contructed a coulometric microdevice based on plug-based microfluidics for the detection of organophosphate pesticides employing acetylcholinesterase and choline oxidase. These enzymes, combined with the substrate acetylcholine, were capable of producing hydrogen peroxide detected at microelectrode array by coulometry. The variation of acetylcholinesterase activity upon addition of organophosphates was detected, with LODs of 33 nM for malathion and 90 nM for acephate and diazinon. This microdevice confirmed to be capable of using very small volume samples, reducing reagent consumption and consenting high reproducibility and sensitivity.

Among organophosphates, nerve agents have been also monitored in the environment due to their capability to inhibit acetylcholinesterase using microfluidic chips. Yoon et al. [180] immobilised acetylcholinesterase by cross-linking with glutaraldehyde and bovine serum albumin on SPE consisting of a cobalt phthalocyanine mediated carbon working electrode, housed within an enzymatic chamber of a microfluidic chip. The substrate acetylthiocholine chloride was fluxed through this chamber undergoing to hydrolysis to produce choline, thus oxidized at the SPE

connected to a potentiostat at a constant applied voltage of 0.1 V. The presented microfluidic biosensor chip showed good repeatability, portability, and feasibility.

Carbofuran and diuron have been determined by using an electrochemical sensor based on cyclic voltammetry coupled to flow injection analysis system [181]. This system showed a linear response in a concentration range between 5.0×10^{-6} and 1.4×10^{-4} M for carbofuran and 5.0×10^{-5} and 1.0×10^{-3} M for diuron, with detection limit of 1.7×10^{-6} M and 2.0×10^{-5} M, respectively. The implemented sensor was applied in soil samples with recovery close to 100%, in accordance with high performance liquid chromatography.

Paraxon, taken as simulant for nerve agents, was determined by means of lab-on-a-chip developed by Arduini et al [182]. The printed biosensor with butyrylcholinesterase as biocomponent was embedded in a cell with microfun for air sampling. The integrated miniaturized circuit was able to apply the potential, to register the current, to turn on-off the fan and eventually give a fast alarm switching on a led (Figure 5A).

Triazine herbicides have been quantified by using a microfluidic chip based on capillary electrophoresis and pulse amperometric detection [183]. In particular, simazine, atrazine, and ametryn were monitored in soil and groundwater by a simple and rapid capillary electrophoresis separation followed by in-channel pulsed amperometric detection within a very short time (seconds). The limit of detection for the sensor was calculated as 0.36, 0.45, and 0.55 nM for simazine, atrazine and ametryn, respectively, with an optimal sample separation and a low electrode fouling.

Phenols have been determined by Liu et al. [184] by means of a three-dimensional graphene incorporated electrochemical sensor. The graphene based sensor was constructed employing polydimethylsiloxane micropillars fabricated in microchannels by photolithography, thus, the surface was modified with 3-aminopropyltriethoxysilane (Figure 5B). The negatively charged graphene oxide sheets were then electrostatically adsorbed on the polydimethylsiloxane micropillar surface, and reduced in the hydrazine vapour. The resultant film provided a conductive working

electrode as well as the support with a large surface area to immobilize tyrosinase enzyme. The target phenol was injected in the microchannel and monitored by amperometry with a detection limit of 50 nM. This microfabricated configuration was able to improve the sensitivity by increasing the surface area for its immobilization and also by the excellent conductivity of graphene.

7. Cross-cutting technologies

Together with the convergence of innovative technologies joint to enhance the performances of biosensors for environmental analysis, newer forefront cross-cutting technologies will have a giant impact on biosensor advances. Technologies like information and communication technology, internet of things, microengineering and 3D printing, organic light emitting diode, and solar cells to name a few, will enable the design of revolutionary devices custom-designed for specific analytical purposes. The future of (bio)sensors is, in fact, entrusted to the fusion of all these technologies in a single embedded device able to satisfy the wide range of analytical requirements associated with a proficient environmental control.

As an example, the concept of wireless connection has facilitated the use of biosensors for in field analysis, permitting to develop networks of sensing systems able to provide a wide-ranging and inclusive control of different environmental compartments. In addition, through the help of the artificial intelligence, analysing the enormous volume of data coming from these sensor networks becomes possible through complex computer models. As an example, Alonso et al. [185] reported a hardware implementation of artificial neural networks using a dsPIC® microcontroller to resolve mixtures of pesticides measured by amperometric acetylcholinesterase biosensors, obtaining prediction ability better than 0.986 compared with those expected for a set of eight external test samples. More recently, Zhao et al. [186] described a system based on acetylcholinesterase biosensor and (the) internet of things for pesticide residue detection and agricultural product traceability. Internet of things is the network of physical objects, including sensor devices,

embedded with electronics, software, and network connectivity that enable them to gather and interchange data [187]. Thanks to the Internet of thing visionary concept, the authors highlighted the benefits of pesticide detection in remote control, obtaining data processing and sharing through detection devices (hypogynous computer) in detection locations. This remote control allowed to extract useful information (e.g. pesticide residue values) for protecting the quality and safety of agricultural products.

Microengineering and 3D printing also represent the ultimate revolution in biosensor fabrication, being able nowadays to allow master manufacturing of homemade and hand-held durable devices [188]. By exploiting 3D printing, the opportunity to construct three-dimensional objects of virtually any shape using powder, plastics, or metals enlarges biosensor benefits thanks to the rapid, simple, and ad hoc prototype manufacturing processes. This chance will lead the 3D printing market to grow at USD 8.41 billion by 2020 [189], since, over the traditional methods, 3D printing offers huge advantages: new combination of different materials, reduced waste, lower costs and time of fabrication. Electrochemistry can surely take advantage from 3D printing in fabricating customised and versatile systems, including handling electrochemical flow cells [190] and extraordinary conductive composites [191]. However, this technology is at its early stage; indeed, even if a number of articles are reported in literature describing the fabrication of chips [192, 193], fluidic devices [194], and microarrays [195], only a few of them have been conceived for environmental application. To report an example, Kudr et al. [196] described the 3D printing fabrication of the electrode holder for the simultaneous electrochemical quantification of Cd^{2+}, Cu^{2+}, and Pb^{2+} ions in different environmental samples.

Microengineering also demonstrated its feasibility in the development of high-tech sensing systems operating with low sample volumes, integrating different analytical functions, and enabling automation. Several technologies have been exploited for sensor microengineering, including electron beam lithography, stencil lithography, nano-imprint lithography, dip pen lithography, or

basic photolithography, providing the mass-production of millimetric sized devices at low cost [197].

In the last years, the organic light-emitting diode (OLED) technology is also gaining momentum due to the distinctive features of diodes as excitation sources, leading to emerging R&D in various applications. An OLED is a light-emitting diode consisting of an organic semiconductor layer positioned between two electrodes capable of emitting light in response to an electric current. Thanks to their amazing attributes, OLEDs have been recently, largely used to create digital displays and portable systems. A major area of research is the development of OLED devices for use in sensing applications [198, 199]. Indeed, satisfactory detection sensitivities and long-term stability can be attained using OLED in sensor design for environmental analysis [200]. A recent example is reported by Tsopela et al. [201] which described the development of a lab-on-chip designed integrating OLED in an electrochemical microsensor for water toxicity analysis. The OLED integrated system demonstrated higher detection capabilities than those using an external white light source for monitoring algal metabolism in presence of herbicides. In particular, O_2 was electrochemically monitored when *Chlamydomonas reinhardtii* green algae were exposed to increasing concentrations of diuron, which was able to provide a concentration-dependent inhibition effect on algae photosynthetic oxygen production rate. The high sensitivity reported (0.48 vs 0.26 nA s^{-1} μM^{-1}) claimed this sensor as a highly promising tool also for further integration of optical and electrochemical transducers enabling double complementary detection.

Lastly, if biosensor systems can be integrated with photovoltaics, it is possible to project sensing platforms that can support themselves by solar energy harvesting with better performance and lower cost. A renewable energy as alternative source of energy, over fossil fuels and nuclear energy, can reduce costs and toxic wastes from battery or electrical power also in biosensor field. This green strategy was adopted by Zhang [202] in fabricating a solar cell power source for biosensing application, based on nanostructures created on a shrink polymer substrate photocathode, demonstrating a 34.1% enhancement of energy conversion efficiency for dye-sensitized solar cells.

In addition, the author stated that these shrink induced micro/nano structures can be tunable in term of conductance, surface wetting ability, and surface morphology, offering well-behaved and versatile applications to detection and energy harvesting with a simple and low cost approach. Also Li et al. [203] highlighted how the integration of biosensors with self-powered systems and communication technology can have a great impact on both lab-on-chip and point-of-care applications.

8. Conclusions and future perspectives

Nowadays, the environment is constantly exposed to an extensive assortment of hazardous chemicals, which affect the quality of air, food, and water, and have consequently enormous influence on human and animal wellbeing. To date, an inclusive picture of the environmental contamination regarding the fate and behaviour of these toxic chemicals still lacks. Therefore, there is an increasing demand for the development of monitoring systems capable of routine and high-throughput analysis to better understand the risk factors associated with adverse environment and human conditions. Moreover, the complex nature of a myriad of contaminants continuously released in the environment requires sophisticated and multipurpose sensing platforms with high grade of selectivity and sensitivity, as well as high capability for in field and continuous analysis. Nevertheless, many chemicals can show dose-response and combination effects further worsening current challenges for their identification and toxicity assessment.

The crucial requirements of sensitivity and selectivity, miniaturisation and portability, cost-effectiveness, fast response, multi-analyte screening for the construction of effective electrochemical devices can be provided only through the convergence of vanguard technologies. Printing technology can be considered a leading technique for electrode preparation to design cost-effective, miniaturised, mass-produced tailored devices. Among printing technologies, screen-printing is the most exploited procedure, even if characterized by a lower resolution. To improve

the resolution, manufacturing techniques as inkjet, sputtering, and roll-2-roll are effective towards the realization of highly-controlled micrometric networks, at the same strength of microfluidics. While the excellence of these methods allows to obtain high-quality electrodes, the fabrication processes require expensive instrumentations making the cost of the final product high. In our opinion, the serigraphic approaches own their greatness in easy application and affordability, allowing to produce electrodes by tailorable procedures, without particular equipment and/or training. Printing technology is also used to produce modified platforms by means of different methods chosen in accordance with the nature of the modifiers, the demanded accuracy, and by the economic resources of the laboratory. We believe that the best technique to modify electrodes is the inkjet-printing because it allows to do not waste material and a common office inkjet-printer, opportunely adapted, could be utilized for this need. This printer allows modifying very tiny areas with a precision of the micrometer range, while, screen-printing the sensing material needs a huge amount of modifiers (i.e. powder) and sometimes the obtainment of such large quantities could be too expensive or unfavourable. The other approaches, electrospinning and electrospraying, represent niche methods to modify electrodes, perhaps too expensive.

Several materials have been exploited as support for screen-printing, including polyester and ceramics. As described in literature, paper, with respect to other materials, has shown high capability to solve some analytical drawbacks of biosensors, including the avoiding the addition of reagents during the measurement. Indeed, by storing all the reagents in the cellulosic network, the end-user is able to perform analysis by simple and handy procedures, without the use of polluting chemicals. This is extremely advantageous, but sometimes the use of paper is not fully exploited. The use of filter paper with its high porosity allows to load all the required reagents/buffers. Instead, the use of office paper does not solve the issue related to the all-in-one platform, but its reduced cost if compared with both plastic and chromatographic paper is an appealing alternative to be exploited toward the realization of eco-friendly sensing platforms for cost-effective environmental analysis, particularly suitable for the developing countries.

Nanomotors have also shown the possibility to move toward the realization of stand-alone platforms for de-centralized environmental surveillance and remediation. The customization of such nano- and micro-objects will conduct to more autonomous systems to be applied in different fields, including remediation, recognition, and sensing, being reagent free and avoiding sample treatment. Nevertheless, drawbacks related to the production of waste (i.e. products, metal release, H^+/OH^-) are still under evaluation, as in the case of the microengines for remediation/detection of pollutants above described, which currently represent the only examples of nanomotors integrated onto a SPE. For this reason, the production of "green" nanomotors represents nowadays the most important challenge in nanomotor design.

Nanomaterial technology similarly demonstrated its powerful contribution i) to improve the electrochemical response as well as the selectivity, ii) to provide a favourable microenvironment for the biocomponents enhancing their stability and sensitivity, and iii) to give a faster measurement if used as a tag to monitor the interactions between the biocomponent and the target analyte. Among the several nanomaterials reported in literature, without any doubt graphene covers an astonishing position over the other nanomaterials. The question is: which will be the next nanomaterial that will tarnish graphene?

At the same strength of nanomaterial technology, biomimetic design has risen as a promising approach having enormous potential to join converging technologies (bioinformatics, genetic engineering, and biotechnology) in solving a wide range of challenges in biosensor fields. Indeed, biomimetic design has proven its potential to project novel bioinspired molecules able to emulate the behaviour of proteins and enzymes with tailored functional and structural features. Artificial molecules, such as aptamers, biomimetics, molecular imprinting polymers, and peptide nucleic acids, are continuously synthesised fostering a trustworthy support to biosensor technology to face typical drawbacks as weak robustness, animal use in bioelement production, and arduous labelling of bioelements with smart tags.

Microfluidics represents a main technology to enhance (bio)sensor performances in terms of sustainability (being able to decrease the use of reagents and the waste volumes), automation, and suitability for in field analysis. Indeed, the potential to convey laboratory set-up instrumentation towards miniaturised and portable sensing systems can lead to overcome main analytical limitations related to the challenging multi-residue analysis, the intrinsic chemical heterogeneity of environmental samples, as well as the requirement for real-time in field measurements. In addition, automation, reduction of reagent costs, and lower amount of chemical waste can be reached through the construction of eco-designed portable devices, which will found significantly improved applications in environmental analysis. As reported in the literature analysed in this review, a number of microfluidics and lab-on-a-chip devices has been conceived taking into account specific analytical claims, and demonstrated the reliability of this technology.

As a result of these interdisciplinary technologies, novel advanced, highly selective and accurate, portable/miniaturized, rapid, and multi-detection sensors will represent an immediate resolution for the main bottlenecks constraining laboratory prototypes to reach real environmental applications.

However, in order to obtain an inclusive picture of the degree of environmental pollution consisting of a comprehensive spatial and temporal distribution of hazardous chemicals, actually, biosensor technology is still solicited by a number of challenges to be tackle. Will vanguard cross-cutting technologies like OLED, 3D printing, internet of things, artificial intelligence, and microengineering be able to furnish outstanding tools so proficient to enable biosensors to take a revolutionary step forward?

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Figure captions

Figure 1: A) Screen-printed onto neoprene wetsuit tissue, in order to create one of the first examples of wearable sensor capable to monitor the safety of the seawater by detecting copper and TNT [Reprinted with permission from reference 33]; **B)** Forensic finger obtained by screen-printing electrode onto a nitrile glove for the detection of gunshot residues and explosives directly on the crime scene [Reprinted with permission from reference 34]; **C)** Fabrication steps for the realization of the reagentless filter paper-based electrochemical phosphate sensor, obtained by using wax patterning, paper chemical modification, and electrode screen-printing [Reprinted with permission from reference 37]; **D)** Procedures followed in the detection of different metal ions after air was sampled. This paper based analytical device allowed to detect lead and cadmium ions by means of anodic stripping voltammetry and iron, nickel, chromium and copper ions with a colorimetric test [Reprinted with permission from reference 39].

Figure 2: A) Scheme of immunosensor for ultrasensitive detection of microcystin-LR exploiting graphene–gold nanocomposite/functional conducting polymer/gold nanoparticle/ionic liquid composite film [Reprinted with permission from reference 89]; **B)** Scheme of the synthesis of graphene oxide–MWCNTs hybrid nanomaterial and its use in the design of sensor for heavy metal ions detection. Inset the digital photos of graphene oxide, MWCNTs and graphene oxide-MWCNTs solutions, respectively [Reprinted with permission from reference 97]; **C)** Scheme of carbon nanotube functionalisation with tyrosinase enzyme for the developing of enzymatic biosensor able to detect phenolic compounds (i.e. catechol) [Reprinted with permission from reference 100].

Figure 3: Scheme of Janus microparticles immobilised on SPE by using a magnetic field are able to produce OH^- that subsequently hydrolyse organophosphorous pesticides in aqueous solution [Reprinted permission with some modifications from reference 160].

Figure 4: A) Illustration of the aptasensor fabrication and the procedure of acetamiprid detection [Reprinted with permission from reference 164]; **B)** Illustrations of the fabrication procedure for the MGO@AuNPs-MIPs [Reprinted with permission from reference 172]; **C)** Principle of the As(III) bioreporter based electrochemical whole-cell based biochip sensor [Reprinted with permission from reference 173].

Figure 5: A) Lab-on-a-chip for nerve agent detection [Reprinted with permission from reference 182]; **B)** Microchannels, 3D graphene micropillar, and patterned electrodes in the electrochemical sensor device [Reprinted with permission from reference 184].

Figures

Figure 1

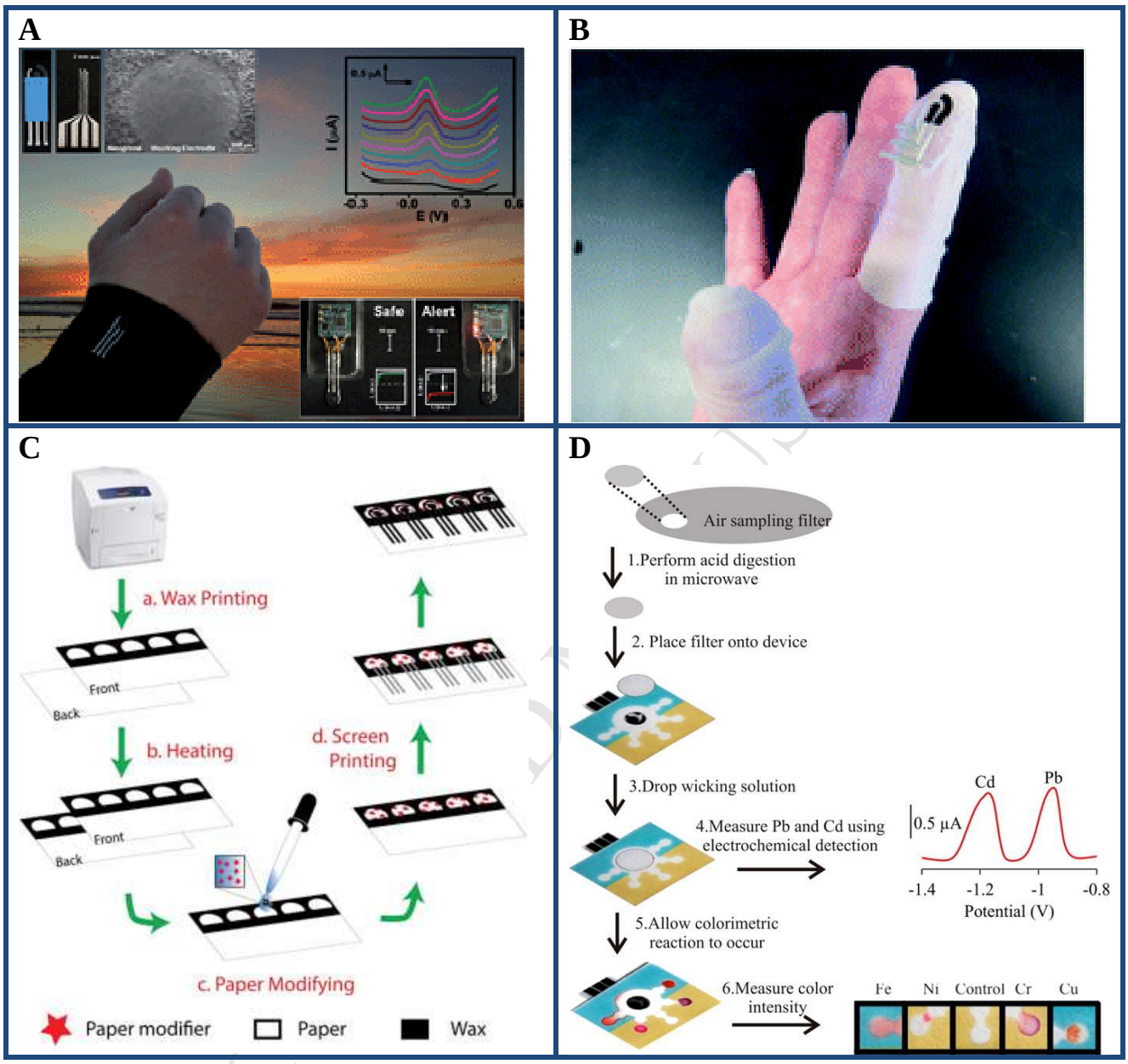


Figure 2

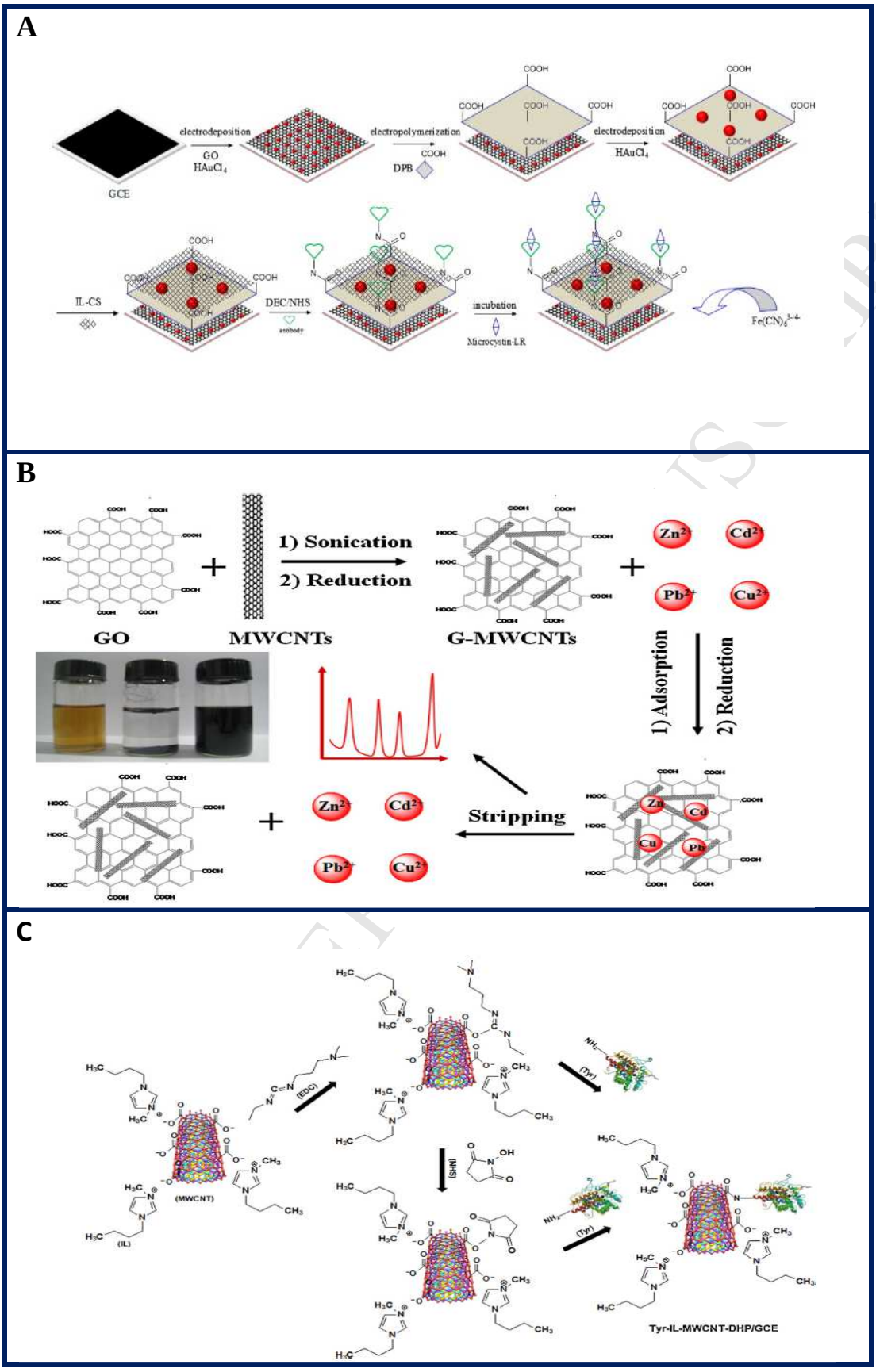

A
GCE
electrodeposition
GO
HAuCl4
electropolymerization
DPB
electrodeposition
HAuCl4
IL-CS
DEC/NHS
antibody
incubation
Microcystin-LR
Fe(CN)6 3-,4-
B
GO
MWCNTs
1) Sonication
2) Reduction
G-MWCNTs
Zn2+
Cd2+
Pb2+
Cu2+
1) Adsorption
2) Reduction
Stripping
C
(MWCNT)
(IL)
(EDC)
(SHN)
(Tyr)
Tyr-IL-MWCNT-DHP/GCE

Figure 3

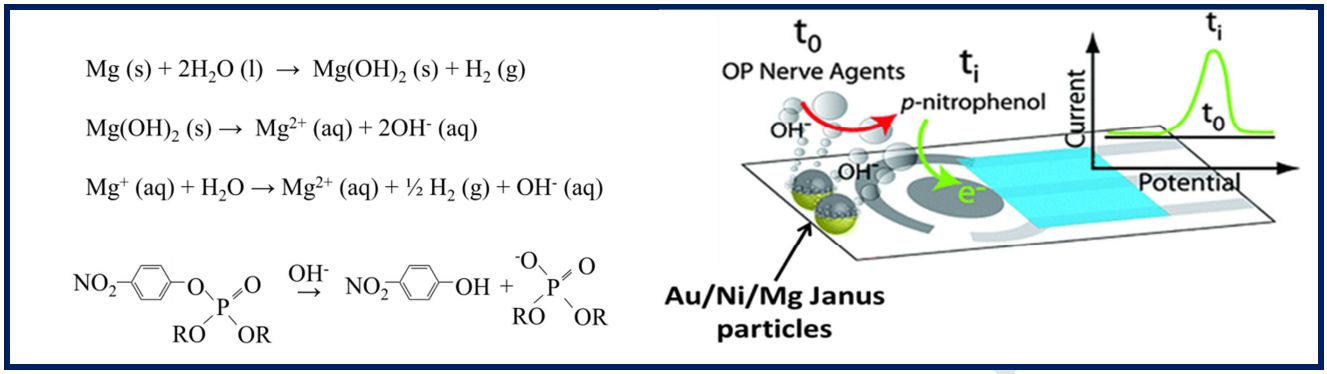


Figure 4

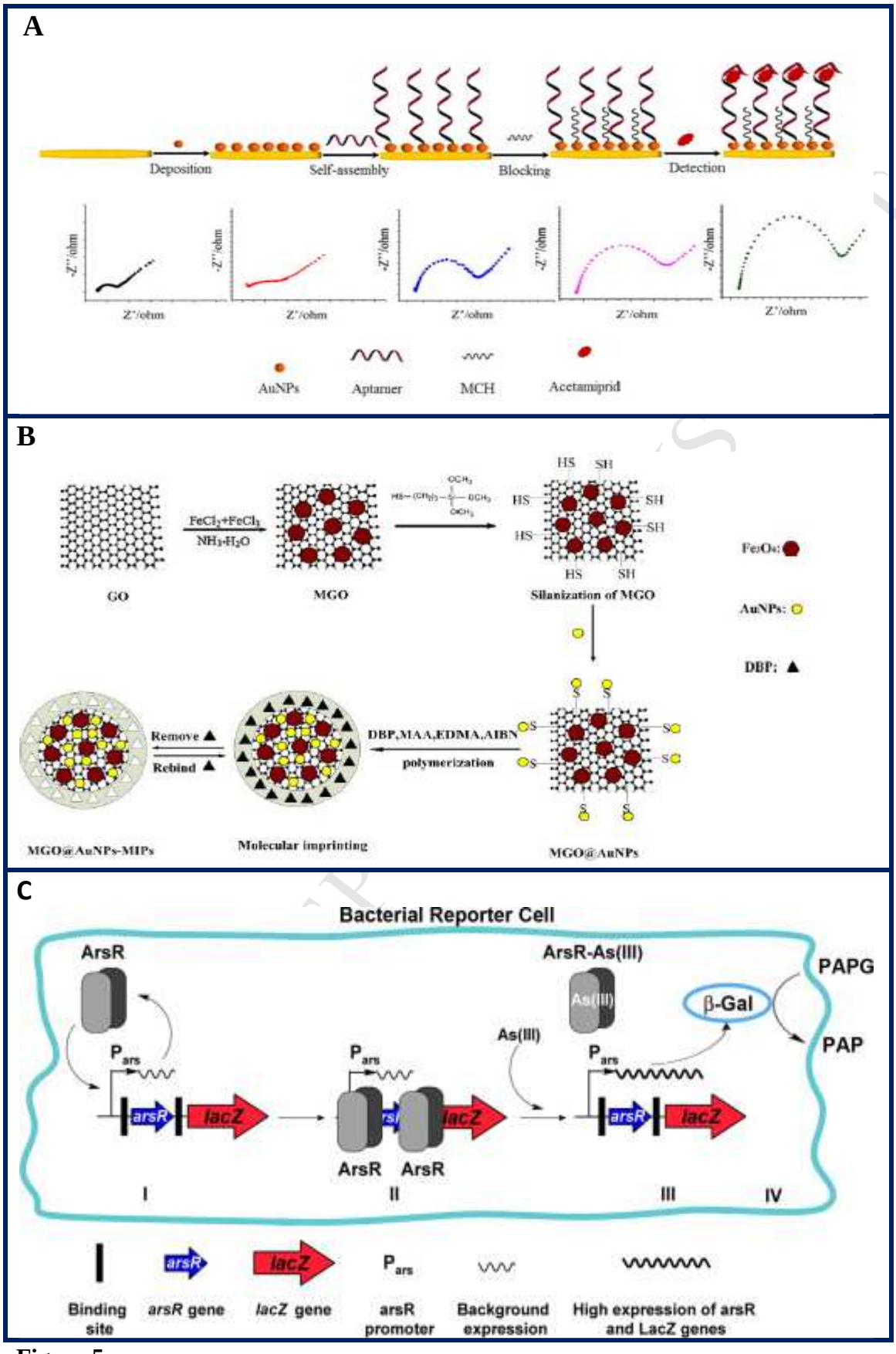
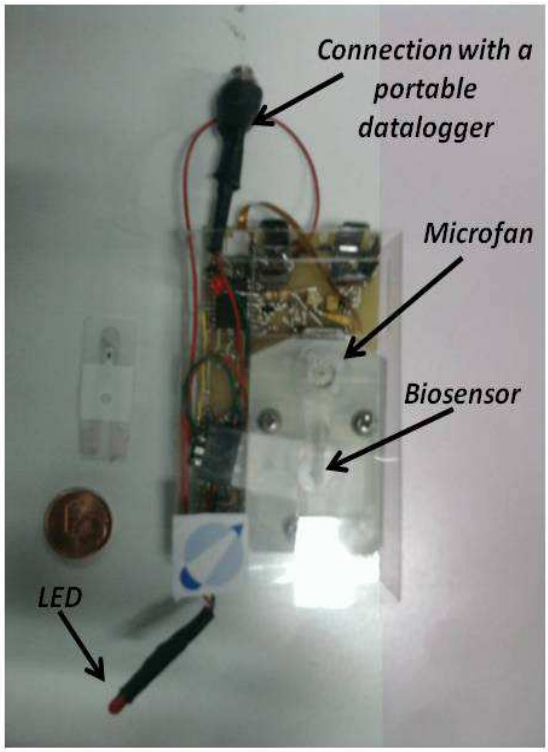


Figure 5

A



B

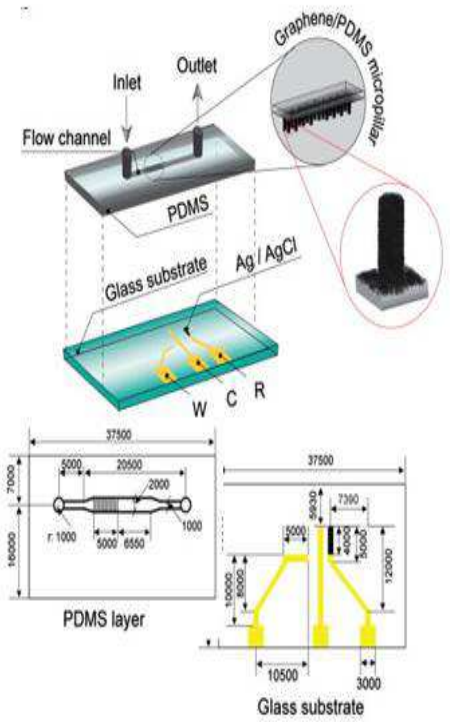


Table 1. Electrochemical (bio)sensors for environmental analysis configured with different nanomaterials.

Pollutants	Working electrode	Linear range	LOD	Sample	Comments	Ref.
Graphene						
Cd(II) Pb(II) Zn(II) Cu(II)	Carbon paste electrode prepared using reduced graphene oxide and bismuth	up to 120 µg L^{-1} up to 120 µg L^{-1} up to 400 µg L^{-1} up to 100 µg L^{-1}	2.8 µg L^{-1} 0.55 µg L^{-1} 17 µg L^{-1} 26 µg L^{-1}	Ground and lake waters	Measurements carried out by using differential pulse anodic stripping voltammetry	[64]
Cd(II) Pb(II)	Glassy carbon electrode modified with Bi and electroreduced graphene oxide-supported thiolated thionine	1-40 µg L^{-1}	0.1 µg L^{-1} 0.05 µg L^{-1}	Spring and river waters	Measurements carried out by using square wave anodic stripping voltammetry	[65]
Catechol Hydroquinone	Glassy carbon electrode modified with graphene and titanium dioxide nanoparticles	0.5-100 µM	0.087 µM 0.082 µM	Lake water	Selective detection of catechol and hydroquinone by differential pulse voltammetry	[68]
Tetracycline	Carbon paste electrode prepared using MWCNTs functionalized with carboxyl groups and graphene oxide	$2.0x10^{-5}$- $3.1x10^{-4}$ M	$3.6x10^{-7}$ M	River water	Measurements carried out by using adsorptive stripping differential pulse voltammetry	[69]
Hydroquinone Catechol p-cresol Nitrite	Glassy carbon electrode modified with reduced graphene oxide and MWCNTs	8.0-391.0 µM 5.5-540.0 µM, 5.0-430.0 µM 75.0-6060.0 µM	2.6 µM 1.8 µM 1.6 µM 25.0 µM	River water	Simultaneous determination using cyclic voltammetry, analytical performances evaluated using differential pulse voltammetry, separately for each compound	[70]
Chlorophenols	Glassy carbon electrode modified with Pd-graphene nanocomposite	4-800 µM	1.5 µM	Waste water	Measurements carried out by using differential	[71]

					pulse voltammetry, this sensor is able to detect chlorophenols, including 2- and 4-chlorophenol	
Tl(I) Pb(II) Hg(II)	Carbon paste electrode prepated with graphene, 1-n-octylpyridinum hexafluorophosphate, and [2,4-$Cl_2C_6H_3C(O)CHPPh_3$]	$1.25x10^{-9}$ - $2.00x10^{-7}$ M	$3.57x10^{-10}$ M $4.50x10^{-10}$ M $3.86x10^{-10}$ M	River water and soil	Simultaneous square wave anodic stripping voltammetric determination of Tl(I), Pb(II) and Hg(II), even in presence of other heavy metals such as Cd(II) and Cu(II)	[72]
Cd(II)	Glassy carbon electrode modified with stannum film/poly(p-aminobenzene sulfonic acid)/graphene	1.0-70.0 µg L^{-1}	0.05 µg L^{-1}	Waste water, lake and farmland irrigation waters	Measurements carried out by using square wave anodic stripping voltammetry	[74]
Methyl parathion	Glassy carbon electrode modified with poly(malachite green)/graphene nanosheets-nafion	0.02-1.5 µM	2.0 nM	River water	Indirectly detection of methyl parathion measuring by chrono-amperometry the product (*p*-nitrophenol) of alkaline hydrolysis	[75]
2-nitroaniline 3-nitroaniline 4-nitroaniline	Glassy carbon electrode modified with graphene and electro-polymerized 7-[(2,4-dihydroxy-5-carboxybenzene)azo]-8-hydroxyquinoline-5-sulfonic acid	0.05-0.60 µg mL^{-1}	0.022 µg mL^{-1}	Sewage	Simultaneous differential pulse voltammetric analysis of the nitroaniline isomer mixtures by principal component regression and partial least squares as calibration	[76]

					methods	
Catechol Hydroquinone	Glassy carbon electrode modified with a composite film of graphene nanosheet and poly(4–vinylpyridine)	0.1-10 µM	26 nM 8.2 nM	Lake water	Selective detection of catechol and hydroquinone by differential pulse voltammetry	[77]
Nonylphenol	Glassy carbon electrode modified with ionic liquid-functionalized graphene nanosheet	0.5-30 µM 30-200 µM	0.058 µM	Soil and river water	Measurements carried out by using differential pulse voltammetry, this sensor was also used to investigate the interaction between nonylphenol and DNA	[78]
17β-estradiol	Glassy carbon electrode modified with reduced graphene oxide and a metal porphyrin	0.1-1.0 µM	5.3 nM	River water	Measurements carried out by using differential pulse voltammetry, the application in real sample did not exhibit any interference of the water matrix	[79]
2-chlorophenol 3-chlorophenol	Carbon paste electrode prepared using β-cyclodextrin functionalised graphene	0.5-40 µM 0.4-77 µM	0.2 µM 0.09 µM	River water	Simultaneous determination of two chlorophenols by differential pulse voltammetry	[81]
Methyl parathion	Glassy carbon electrode modified with electrochemical reduced β-cyclodextrin dispersed graphene	0.3-1.0 µg L^{-1} 1.0-500 µg L^{-1}	0.05 µg L^{-1}	Sea water	Detection by exploiting the adsorption properties of the nanocomposite, measurements by differential pulse voltammetry in absence of oxygen	[82]

Methyl parathion Carbofuran	Glassy carbon electrodes modified with carboxylic graphene, SnO_2 nanoparticles, and Nafion and AChE	10^{-13}-10^{-10} M 10^{-10}-10^{-8} M 10^{-12}-10^{-10} M 10^{-10}-10^{-8} M	$5x10^{-14}$ M $5x10^{-13}$ M	Lake water	Detection by exploiting methyl Parathion/ Carbofuran capability to inhibit AChE, measurements carried out by using cyclic voltammetry	[84]
Dichlorvos	Glassy carbon modified with electrochemically reduced graphene oxide and Nafion hybrid nanocomposite and AChE	5.0-100 ng mL^{-1} 1.0-20 µg mL^{-1}	2.0 ng mL^{-1}	River water	Detection by exploiting Dichlorvos capability to inhibit AChE, measurements carried out by using amperometry	[87]
Catechol	Glassy carbon electrode modified with TiO_2 nanotubes grown on graphene nanoplatelets, Nafion, and tyrosinase	0.30-110 µM 110.5-390 µM	0.055 µM	River water	Biosensor using tyrosinase as biocomponent, detection by chrono-amperometry	[88]
Microcystin-LR	Glassy carbon electrode modified with graphene oxide combined with gold nanoparticles, 2,5-di-(2-thienyl)-1-pyrrole-1-(p-benzoicacid) polymer, ionic liquids, and microcystin-LR antibody	$1.0x10^{-16}$ - $8.0x10^{-15}$ M	$3.7x10^{-17}$ M	Lake, river, and ground waters	Biosensor using polyclonal antibody as biocomponent. Microcystin-LR detection evaluating the response of ferro/ferri cyanide by differential pulse voltammetry	[89]
Carbon nanotubes						
Methyl parathion	Glassy carbon electrode modified with nanocomposite constituted of MWCNTs–CeO_2–gold nanoparticles	$1.0x10^{-10}$ - $1.0x10^{-7}$ M	$3.02x10^{-11}$ M	River water and soil	Measurement carried out by differential pulse voltammetry	[96]
Cd(II)	Carbon paste electrode prepared using MWCNTs and octylpyridinum hexafluorophosphate	0.2-23 µg L^{-1}	0.08 µg L^{-1}	Waste water and Persian gulf water	Measurement carried out by differential pulse anodic stripping	[98]

					voltammetry	
Hg(II)	Carbon paste electrode prepared using 1-n-butyl-3-methylimidazolium tetrafluoroborate, 1-(2-ethoxyphenyl)-3-(3-nitrophenyl)triazene and MWCNTs	$5.09x10^{-9}$ - $1.0x10^{-4}$ M	$2.5x10^{-9}$ M	Sea and river waters	Potentiometric measurement, Nernstian slope of 29.3 ± (0.2) mV decade^{-1} of Hg(II)	[99]
Cd(II) Hg(II)	Carbon paste electrode prepared using CNTs and Chitosan	$5.9x10^{-8}$ - $1.5x10^{-6}$ M $6.7x10^{-9}$ - $8.3x10^{-8}$ M	$9.8x10^{-9}$ M $2.4x10^{-9}$ M	Waste water and sediments	Cd(II) and Hg(II) were evaluated by using linear sweep anodic stripping voltammetry	[100]
Methyl parathion	Glassy carbon electrode modified with MWCNTs–poly(acrylamide)	$5.0x10^{-9}$ - $1.0x10^{-5}$ M	$2.0x10^{-9}$ M	River water	Measurements carried out by using differential pulse voltammetry in absence of oxygen	[101]
Pb(II) Cd(II)	Glassy carbon electrode modified with poly-sodium 4-styrenesulfonate with CNTs and in situ bismuth film	0.5-90 µg L^{-1} 0.5-50 µg L^{-1}	0.04 µg L^{-1} 0.02 µg L^{-1}	Lake water	Measurements carried out by using differential pulse anodic stripping voltammetry	[102]
Catechol	Glassy carbon electrode modified with MWCNTs, 1-butyl-3-methylimidazolium chloride, dihexadecylphosphate, and tyrosinase	$4.9x10^{-6}$ - $1.1x10^{-3}$ M	$5.8x10^{-7}$ M	Lake water	Biosensor using tyrosinase as biocomponent, measurements performed by using linear sweep voltammetry	[103]
Carbon black						
Hg(II)	SPE modified with CB N220	$2.5x10^{-8}$ - $1x10^{-7}$ M	$5x10^{-9}$ M	Drinking water	Amperometric detection by exploiting the reaction between thiocholine and Hg(II)	[116]
Paraoxon	SPE modified with CB N220, Nafion, bovine serum	up to 30 µg L^{-1}	5 µg L^{-1}	Waste water	Detection by exploiting Paraoxon	[117]

	albumin, glutaraldehyde, and BChE				capability to inhibit BChE, measurements carried out by using amperometry	
Phosphate	SPE modified with CB N220	0.5-100 µM	0.1 µM	River and aquarium waters	Phosphate was measured using amperometric technique via electrochemical reduction of molybdo-phosphate complex	[118]
As(III)	SPE modified with CB N220 and gold nanoparticles	2-30 µg L^{-1}	0.4 µg L^{-1}	Drinking water	Measurements carried out by using linear sweep anodic stripping voltammetry	[58]
Hg(II)	SPE modified with CB N220 and gold nanoparticles	up to 60 µg L^{-1} 60-100 µg L^{-1}	3 µg L^{-1}	Soil and river waters	Measurements carried out by using square wave anodic stripping voltammetry	[59]
Paraoxon	SPE modified with CB/cobalt Phthalocyanine, Nafion, bovine serum albumin, glutaraldehyde, and BChE	up to 110 nM	18 nM	Wastewater	Detection by exploiting Paraoxon capability to inhibit BChE, measurements carried out by using amperometry	[119]
Other carbonaceous nanomaterials						
Catechol Hydroquinone	Carbon paste electrode modified with electrospun carbon nanofibers	1-200 µM	0.2 µM 0.4 µM	Lake water	Selective detection of catechol and hydroquinone by differential pulse voltammetry	[121]
Hg(II) Pb(II)	SPE modified with carbonaceous nanospheres and polypyrrole	5-35 nM 1-7 nM	0.0041 nM 0.0214 nM	Ground water	Measurements carried out by using square wave anodic stripping voltammetry	[123]
2,4-	Glassy carbon	0.4-8.0 µM	0.01 µM	Lake		[124]

dichlorophenol	electrode modified with a nanocomposite constituted of carbon dots, hexadecyltrimethyl ammonium bromide, and chitosan			water	Measurements carried out by using differential pulse voltammetry	
Metallic nanoparticles based nanomaterials						
Hydroquinone	Carbon paste electrode prepared using gold nanoparticle and graphene composite film and carbon ionic liquid	0.06-800.0 µM	0.018 µM	Synthetic waste water	Hydroquinone detection by using differential pulse voltammetry, catechol did not interfere	[125]
2,4,6-trinitrotoluene 2,4-dinitrotoluene Tetryl	Glassy carbon electrode modified with gold nanoparticles and poly(ophenylenediamine-aniline film)	2.5-40 mg L^{-1} 2-40 mg L^{-1} 5-100 mg L^{-1}	2.1 mg L^{-1} 1.28 mg L^{-1} 3.8 mg L^{-1}	Real post-blast residual samples	Measurements carried out by using cyclic voltammetry	[126]
Zn(II) Cd(II)	Gold electrode modified with gold nanoparticles, cysteine, and dipicolinic acid	0.020-25 µM 0.045-17.0 µM	0.008 µM 0.015 µM	Lake, river, and spring waters	Measurements carried out by using differential pulse anodic stripping voltammetry	[127]
As(III)	Glassy carbon electrode modified with gold-nanoparticle-embedded nafion composite	0.1-12 µg L^{-1}	0.047 µg L^{-1}	Lake water	Measurements carried out by using square wave anodic stripping voltammetry, EDTA was used to overcome Cu(II) and Hg(II) interference	[128]
Hg(II)	Carbon paste electrode designed by incorporation of thiolated amino acids capped gold nanoparticles into the carbon ionic liquid	10 nM-20 µM	2.3 nM	Waste water	Hg(II) was detected exploiting the chelating ability of the nanocomposite combined with square wave	[129]

					voltammetry	
As(III)	Glassy carbon electrode modified with silver nanoparticle and chitosan	10-100 µg L^{-1}	1.20 µg L^{-1}	Ground water	Measurements carried out by using differential pulse anodic stripping voltammetry	[130]
Catechol	Indium Tin Oxide electrode modified with tyrosinase, sol-gel and polyvinylpyrrolidone stabilized gold nanoparticles	$1.0x10^{-6}$ - $6.0x10^{-6}$ M	$3x10^{-7}$ M	Water	Biosensor using tyrosinase as biocomponent, detection by amperometric technique	[133]
Phenol	SPE modified with gold nanoparticles and tyrosinase	up to 15 mg L^{-1}	47 µg L^{-1}	Ground water	Biosensor using tyrosinase as biocomponent, detection by square wave voltammetry	[134]
Microcystin-LR	Glassy carbon electrode modified with gold nanoparticles/ silicon template/ methylene blue/chitosan nanocomposite- and antibody	0.5 ng mL^{-1} - 25 µg mL^{-1}	0.1 ng mL^{-1}	Ground water	The decrease in differential pulse voltammetry responses was observed with increasing concentrations of Microcystin-LR due to the formation of immuno-complexes (Microcystin-LR/ anti-Microcystin-LR antibodies)	[135]
Other nanomaterials						
Pb(II)	SPE modified with mesoporous silica nanoparticles	1-30 µg mL^{-1}	0.1 µg mL^{-1}	River and ground water	Measurements carried out by using square wave anodic stripping voltammetry	[138]
Pb(II) Cd(II)	Glassy carbon electrode modified with mesoporous silica nanoparticles and bismuth film	2-150 µg mL^{-1}	0.2 µg L^{-1} 0.6 µg L^{-1}	Lake water	Measurements carried out by using square wave anodic stripping voltammetry	[139]

Methyl parathion Carbaryl	Glassy carbon electrode modified with AChE, carboxylic silica nanosheets, platinum nanoparticles, and Nafion	$1.0x10^{-12}$ - $1.0x10^{-8}$ M	$5.52x10^{-13}$ M $5.65x10^{-13}$ M	Lake water	Detection by exploiting Methyl parathion/ Carbaryl capability to inhibit AChE, measurements carried out by using cyclic voltammetry	[140]
Hg(II)	Carbon paste electrode preapared using carbon paste, mineral oil, and mesostructured silica nanoparticles functionalized with a 5-mercapto-1-methyltetrazole derivative	0.025-0.25 µM	0.023 µM	Ground water and river water	Measurements carried out by using square wave anodic stripping voltammetry	[141]
Phenolic compounds	Au electrode modified with tyrosinase and hydroxyapatite nanoparticles-chitosan nanocomposite	10 nM-7 µM	5 nM	Waste water	Biosensor using tyrosinase as biocomponent, detection by amperometry	[142]
Methyl parathion	Carbon paste electrode prepared using graphite powder, paraffin oil, and ZrO_2 nanoparticles	5-3000 µg L^{-1}	2 µg L^{-1}	River water	Measurements carried out by using square wave voltammetry	[143]
Cd(II) Pb(II) Cu(II)	Glassy carbon electrode modified with molybdenum-chalcogenide-halide nanowires	0.5-150 µg L^{-1} 1.5-450 µg L^{-1} 1.5-450 µg L^{-1}	0.10 µg L^{-1} 0.45 µg L^{-1} 0.20 µg L^{-1}	Water	Measurements carried out by using differential pulse anodic stripping voltammetry	[144]
Pentachloro-phenol	Glassy carbon electrode modified with $CdSe_xTe_{1-x}$ nanocrystal/ TiO_2nanotube	1 nM-0.3 µM	1 pM	River water	Measurements carried out by using differential pulse anodic stripping voltammetry	[145]

Bi: bismuth; AChE: acetylcholinesterase; MWCNTs: multi-walled carbon nanotubes; CNTs: carbon nanotubes; CB: carbon black; BChE: butyrylcholinesterase.

Highlights

- Cutting-edge technologies in biosensor fabrication for the detection of pollutants.
- Printed sensors, nanomaterials, nanomotors, biomimetic design, lab on a chip are described.
- Futuristic cross-cutting technologies for innovative aspects of (bio)sensors are reported.

Author Biography

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Danila Moscone is full Professor of Analytical Chemistry. Prof. Moscone’s activity concerns the construction of different biosensors and its application in analytical matrices since thirty years. During this time, she improved her experience in the field of electrochemical sensors and flow systems coupled to biosensors. The research activity carried out was published in several papers as follows: 30 chapters on books, 2 reviews, 1 monograph, 137 papers on international and national scientific journals, 2 patents, 36 proceedings, 2 videos, more than 300 oral and poster presentations at scientific meetings. Her H-index is 36, with 3806 total citations (Scopus, April 2016).

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Stefano Cinti

Viviana Scognamiglio

Danila Moscone

Giuseppe Palleschi