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Review—Electrochemical Sensors for Determination of the Endocrine Disruptor, Bisphenol A

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Bisphenol A is an organic compound, belonging to the group of diphenylmethane derivates and is worldwide used in the fabrication of plastic and some resins. It leaches from plastic products and affects the environment and mostly the human body. BPA is known to be a xenoestrogen that mimics the role of hormones in the human body and disturbs the endocrine and reproductive systems. High doses are correlated with many disorders of the reproductive system. Being an electro-active molecule, it was intensively studied using electrochemical sensors with applications in food industry, environmental field and biomedical field. This review covers a big number of papers that had studied the electro oxidation of BPA from real samples using different types of electrochemical sensors.

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Plastic waste disposal in the environment can cause release of a lot of toxic and pollutant materials, which can affect the health of the human body, especially children and infants. This kind of chemicals are known as endocrine disrupting chemicals (EDCs), responsible for tricking the endocrine system into releasing high levels of hormones in the body. These high levels of hormones are present in many disorders that affect the reproductive system, such as precocious puberty, infertility, birth defects, tumours, polycystic ovaries and so on.

Bisphenol A (BPA) is one of the most studied EDCs and it is widely used in the fabrication of polycarbonate, epoxy resins, as fixing material in the fabrication of polyvinyl chloride (PVC)[1] and as intermediary material in plastic manufacturing. Mainly used household items that may contain a high level of BPA are: soda and food cans, cosmetics, baby plastic bottles and so on (Figure 1).

Many research teams have been centred their attention on developing the fast and cheapest method for determination of BPA from food, plastics, water or biological samples. Even though there are many analytical techniques for analysis of BPA,[2–6] this review was focused on the electrochemical methods and on the electrochemical sensors used for the quantitative assessment of BPA from real samples. In the last years, electrochemical sensors used for the determination of BPA[7–10] proved to be a great alternative to classical methods, due to their high sensitivity, good selectivity, cheap materials required small amounts of solutions, solvents and real samples, no need for skilled personnel and no pre-treatment of real samples.

Electro-Oxidation Products–Fouling Effect

BPA is an electroactive molecule, but being a phenolic compound, the direct electrochemical oxidation of BPA is not easily achieved. The formation of secondary oxidation products fouls the electrode system. On the surface of an unmodified electrode the process is irreversible and needs an overpotential,[11] aspect that diminishes the sensitivity of the method.

In the direct electro-oxidation process of BPA are involved two electrons and two protons and the reaction products obtained are mainly phenoxy radicals and quinone.[12] The reaction mechanism is based on the oxidation of the aromatic ring from BPA structure (Figure 1) to phenoxonium ions or phenoxy radical ions. During electrochemical measurements these radical ions become subject to the polymerization process (see Fig. 2) and form an insulating film on the electrode surface area, affecting the further electro-oxidation of BPA.[13] This mainly drawback of the electrochemical determination of BPA was consequently studied and anti-fouling materials were used in the design of the electrochemical sensors employed for determination of BPA. The anti-fouling modifying materials such as surfactants;[13–15] n hexyl–methylimidazolium hexafluoro phosphate,[16] other ionic liquids[17–19] and 6-mercapto-1-hexanol[21] were discussed independently in the following chapters.

The author intensively reviewed several recent papers (mainly since 2010) on sensors, aptasensors and biosensors developed for the detection of BPA, emphasizing the limit of detection, selectivity, stability and analytical applications. BPA determination by electrochemical sensors had attracted numerous studies, and the author wants to apologize to the authors of those papers that were not included in this review.

Applications

Glassy-carbon electrodes for determination of bisphenol A.— The glassy carbon electrode was widely used for decades for electrochemical determination of various compounds. The GCE surface is easily modified for a more selective and sensitive analysis. For the determination of BPA from real samples a lot of modified GCEs were fabricated (see Table I).

In 2010, the electrochemical behavior of BPA was examined on Mg–Al-CO_3 layered double hydroxide (LDH) modified GCE, by Yin and co-workers. The presence of a metal cation, M^{3+}, leads to a higher positive charge density of brucite-like layers and a LDH is interesting, mostly, due to its ease of preparation, large surface are and good catalytic and adsorption properties. The limit of detection was 5.0×10^{-9} mol L^{-1}, and in the interference studies, 50-fold concentration

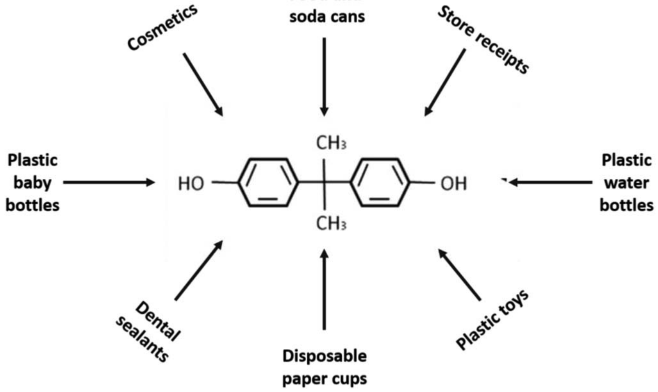

Figure 1. Environmental sources of contamination with BPA.

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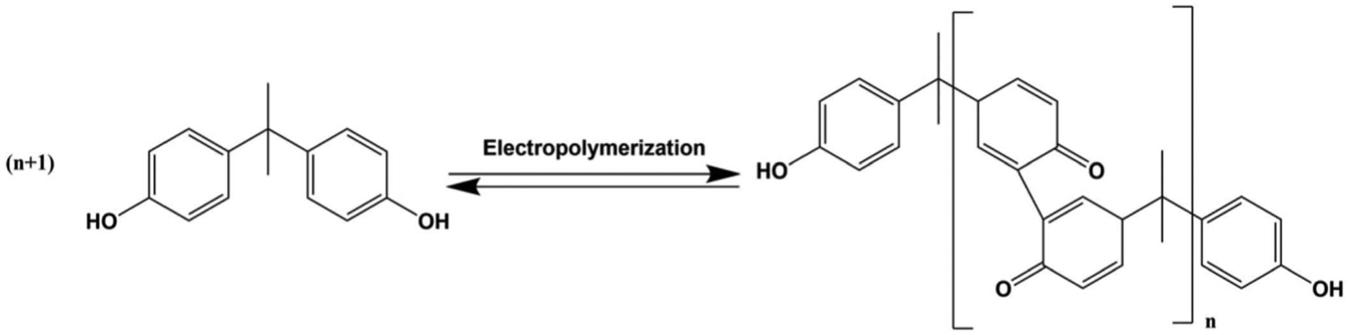


Figure 2. Schematic illustration of bisphenol A electro-oxidation mechanism (Copyright permission from the publisher "The Electrochemical Society").

of Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-} and NO^{3-} have no influence on the determination of BPA. Other phenolic compounds showed different oxidation peaks than BPA. Recovery percentage of BPA from plastic samples was between 96% and 105%.[21]

Fan et al. developed an electrochemical sensing platform based on nitrogen-doped graphene sheets (N-GS) and chitosan (CS) modified GCE which has favourable electron transfer ability and electrocatalytic properties, which enhance the response toward oxidation of BPA. The BPA concentration range covered was from 1.0×10^{-8} – 1.3×10^{-6} mol L^{-1} with a limit of detection of 5.0×10^{-9} mol L^{-1} obtained under optimal conditions. The authors fabricated 10 modified GCEs to prove the reproducibility of the method and the RSD value was 4.8%. For selectivity studies, 1.0×10^{-6} mol L^{-1} BPA was mixed with solutions of 2,5-dinitrophenol, 2,4-dinitrophenol, p-nitrophenol (100-fold concentration) and were evaluated, showing no influence in current intensity in the oxidation of BPA. The proposed modified GCE showed satisfactory results for the determination of BPA from river water samples, recovery percentage in the range of 95.8% to 106.5%.[22]

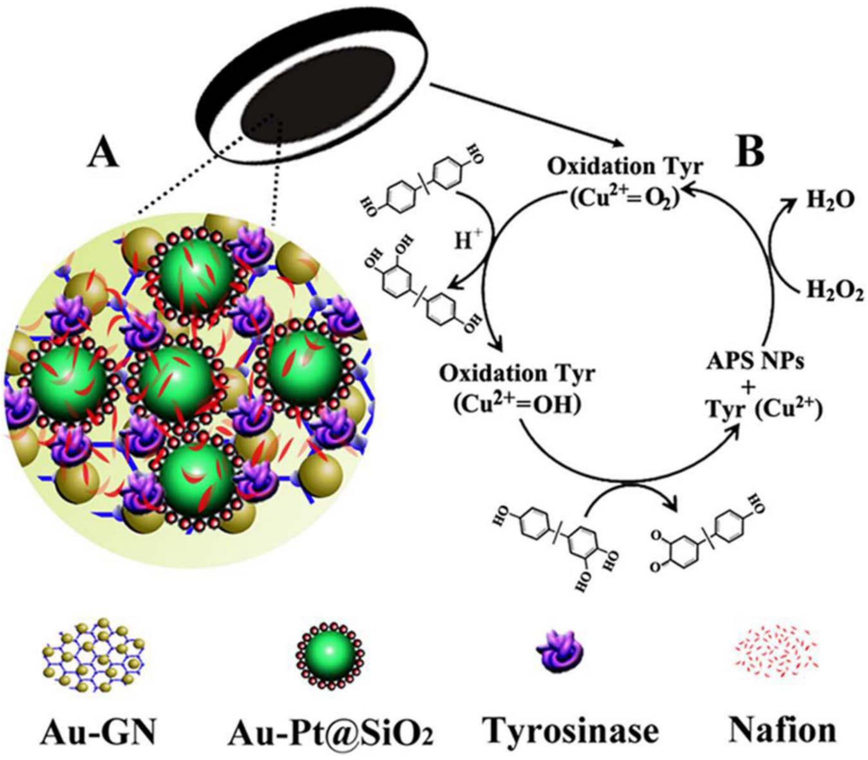
New graphene–silk peptide (Gr–SP) nanosheets were prepared and successfully fabricated with tyrosinase (Tyr) as a biosensor used for the determination of three types of phenolic compounds, one of them being BPA. Tyr was immobilized on top of Gr-SP nanosheets through the covalent cross-linking of amine group in SP and Tyr with glutaraldehyde. The linear concentration range and the correlation coefficient of BPA on the proposed biosensor was 2.0×10^{-9} – 5.5×10^{-6} mol L^{-1} ($R = 0.9988$). The limit of detection was calculated to be 7.2×10^{-10} mol L^{-1}. The reproducibility of the method was investigated by recording the amperometric response for five successive additions of the same concentration of BPA with an RSD of 3.85% and by preparing 6 new Gr–SP–Tyr/GCEs and used for the determination of a solution of 2.0 × 10–7 mol L-1, with an RSD of 4.6%. After one-month storage (in the refrigerator at 4°C), the initial response of the biosensor decreased with 6.4%. 1:1 concentration ratio of BPA and the following interfering species: vitamin C, uric acid, m-dihydroxybenzene, p-nitrophenol showed no interference in the recording of the amperometric signal of BPA, while dopamine, catechol and phenol showed positive interference on the determination of BPA. The practical utility of the proposed biosensor was investigated by measuring the concentration of BPA from a plastic drinking bottle and the result was in good agreement with HPLC method.[23]

Huang et al. were the first to prepare an electro-active graphene oxide (GO) nanocomposite by covalently grafting 4-ferrocenylethyne-phenylamine ($Fc-NH_2$) onto the surface of GO. The nanocomposite was coupled with $HAuCl_4$ and simultaneous electrodeposited on top of GCE, forming $rGO-Fc-NH_2/AuNPs/GCE$. The covalently grafted material formed a film that can effectively prevent the electron mediator leaking from the electrode surface. The addition of gold nanoparticles (AuNPs) diminished the value of charge transfer resistance ($Rct = 25$ Ω) obtained on bare GCE (560 Ω) and on $rGO-Fc-NH_2/GCE$ (250 Ω). This sensor showed linearity response from 5.0×10^{-9}–1.0×10^{-5} mol L^{-1} with the detection limit of 2.0×10^{-9} mol L^{-1}. For seven determinations in a row the RSD for the oxidation peak currents of BPA was 3.1%, indicating excellent repeatability of the modified GCE. The oxidation peak current for 2.0×10^{-6} mol L^{-1} BPA in the absence and presence of different concentrations of interfering species were investigated. 100-fold concentrations of hydroquinone, hydroxyphenol, pyrocathecol and 4-nitrophenol and 200-fold concentrations of K^+, Na+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, Cl^-, NO^{3-} and SO_4^{2-} had no influence on the signals of BPA. Recovery values from 96.0% to 106.0% were obtained from different milk samples.[24]

Pan et al. prepared graphene-gold nanoparticles composite material by introducing gold nanoparticle to separate individual graphene

Table I. Modified glassy carbon electrodes used for voltammetric determination of BPA.

Glassy carbon electrode modified with:	Limit of detection (mol L^{-1})	Samples	Reference
LDH	5.0×10^{-9}	Plastic products	21
N-GS/CS	5.0×10^{-9}	River water	22
Gr–SP–Tyr	7.2×10^{-10}	Plastic bottles	23
$rGO-Fc-NH_2/AuNPs$	2.0×10^{-9}	Milk	24
GR/Au-Tyr-CS	1.0×10^{-9}	Plastic cups Milk Cartons	25
Tyr/APS/Au-GN	1.8×10^{-6}	Olive oil extracts and chips samples	26
Aptamer-NPGF	5.6×10^{-11}	Serum samples	27
Cu_2O-rGO	5.3×10^{-8}	Water samples	28
Cu-Zn/GO	8.8×10^{-10}	baby feeding bottle, pacifier, water bottle, food storage, container samples	29
MnP/PANI-PMMA-TiO_2	1.7×10^{-10}	-	30
Anti-BPA/AuNPs/N-S-P-CDs	5.3×10^{-10}	-	31



Scheme 1. (A) Illustration for the construction of Tyr enzyme biosensor based on Try/APS/Au-GN NCs. (B) Possible oxidation process of BPA on the developed electrochemical sensor (Copyright permission from the publisher "The Electrochemical Society").

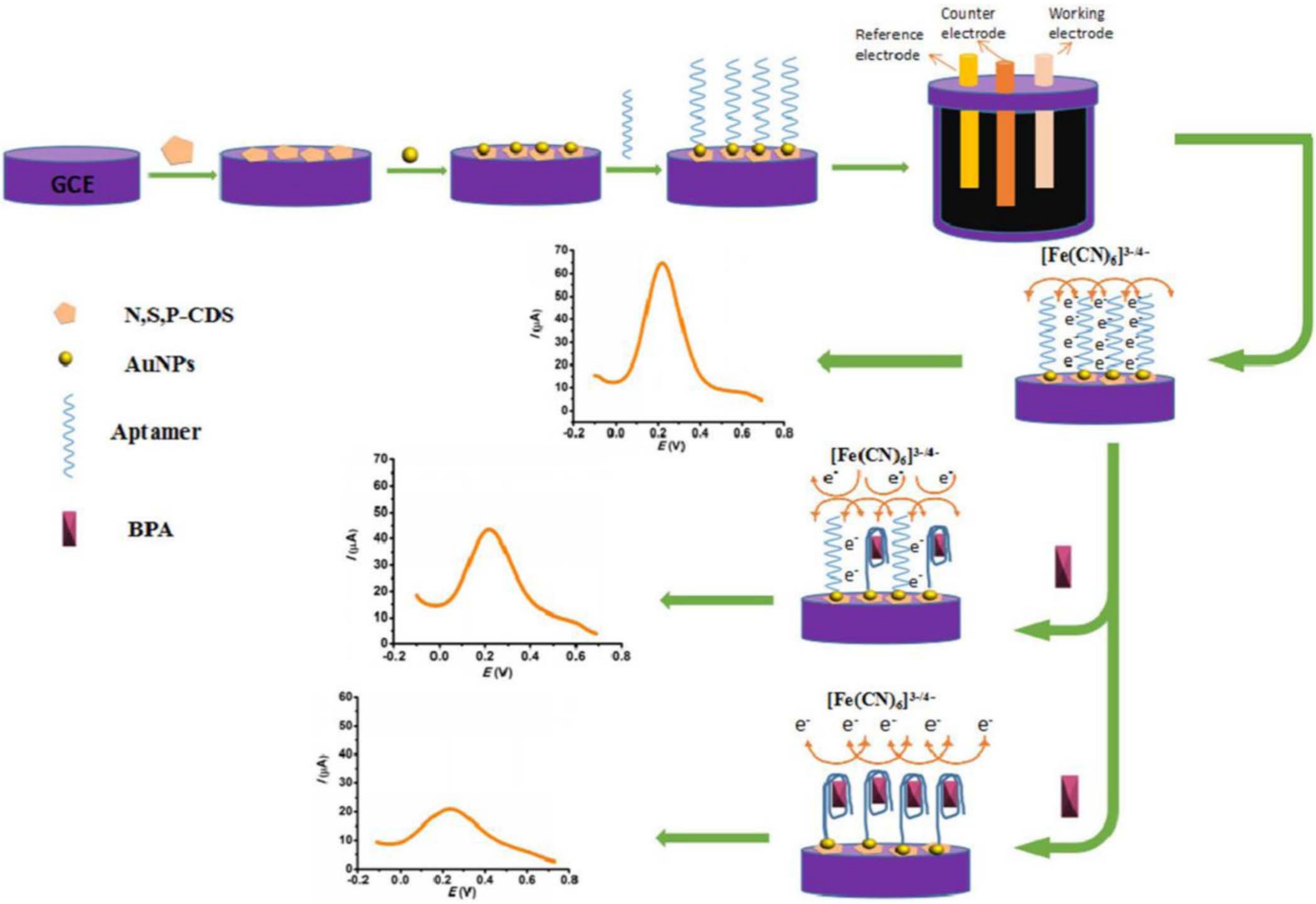
sheets. This fabricated nanocomposite was used as support material for the construction of a tyrosinase biosensor for determination of BPA which proved to be a reliable tool for rapid on-site analysis regarding pollution affairs. Even if the addition of chitosan and tyrosinase hindered the transfer of electrons, without them the redox current does not appear. The sensitivity of the GR/Au-Tyr-CS/GCE was 3.59 mA mol L^{-1}. The stability of the biosensor was tested after 90 days, showing a RSD value of 7.3% in current intensities. The proposed biosensor was used to analyze BPA levels from plastic cups and milk carton samples showing a recovery range from 98.2% to 110.7%, and the corresponding RSD ranged from 4.3 to 6.1%. To the author's knowledge, this paper is the first to report the reduction of BPA.[25]

Wu et al. also incorporated Tyr with Au-Pt@SiO_2 nanospheres (APS) and casted the nanocomposite on GCE via the electrostatic interaction and van der Waals force. The Au-Pt nanoparticles were dopped on top of the SiO_2 nanospheres, to solve the low conductivity issue presented by the SiO_2. To provide a better microenvironment for Tyr to keep its stability and bioactivity the authors added gold nanoparticles modified graphene nanosheets (Au-GN) on the GCE. The modification process of GCE with the Tyr/APS/Au-GN nanocomposite is depicted in Scheme 1. The detection limit reached using this enzyme biosensor was 1.8×10^{-6} mol L^{-1}. The stability of the biosensor was tested after 56 days, showing a RSD value lower than 5.0%. This proposed biosensor is less stable than the one described above, GR/Au-Tyr-CS/GCE.[25] The selectivity of the method is discussed using the phenolic compounds phenol, hydroquinol and resorcinol, which show a slightly interference toward the oxidation of BPA. Olive oil extracts and chips samples were used for the analytical application of the method. The recovery percentages were between 87.4% and 110.7%.[26]

In 2015, Zhu and co-workers reported a biosensor based on 5'-thiolated DNA aptamer (50-CCG GTG GGT GGT CAG GTG GGATAG CGT TCC GCGTAT GGC CCA GCG CAT CAC GGGTTC GCA CCA-30) that is specific to BPA. The aptamer was immobilized on top of a nano porous gold film (NPGF) modified GCE. The limit of detection was very low 5.6×10^{-11} mol L^{-1}. The proposed biosensor was very selective toward the determination of BPA, when other interfering species were added to the electrochemical cell. For 10-fold concentration of phenol, hydroquinone, 4,40-dihydroxybiphenyl, and bisphenol B, the developed biosensor did not show noticeable redox peaks. A good electrode-to-electrode reproducibility was achieved with an RSD value of 6.2%. Also, a good stability is reported, for more than two months, which is due to the inherent chemical stability of NPGF and aptamer, as well as the powerful bond between gold and thiol functional group of the aptamer. This biosensor was employed successfully for detection of BPA from human serum samples.[27]

A GCE was modified with cuprous oxide (Cu_2O) - reduced graphene oxide nanocomposite for determination of BPA from water samples such as lake water, bottled and tap water. The detection range was from 1.0×10^{-7} to 8.0×10^{-5} mol L^{-1} and the limit of detection of 5.3×10^{-8} mol L^{-1}. The RSD value of the proposed sensor was 5.8% for 7 measurements of 0.1 μmol L^{-1}, showing high precision and a 14 days stability with 90% stability in the original results. Inorganic ions: Na^+, OH^-, Cl^-, Ba^{2+}, Cu^{2+}, Ca^{2+}, Fe^{3+}, and possible organic interfering compounds, such as phenol, hydroquinone and three types of bisphenols showed no interference for BPA sensing. The recovery percentage of BPA from water samples using the Cu_2O-rGO/GCE was higher than 98%.[28]

In 2019, Karabiberoglu reported a copper oxide-zinc oxide/graphene oxide nanocomposite (Cu-Zn/GO) modified GCE for determination of BPA from baby feeding bottle, pacifier, water bottle, food storage, container samples. The proposed Cu-Zn/GO/GCE displayed two linear concentration ranges for determination of BPA: 3.0×10^{-9} mol L^{-1} – 1.0×10^{-7} mol L^{-1} and 3.5×10^{-4} mol L^{-1} – 2.0×10^{-2} mol L^{-1} and with 8.8×10^{-10} mol L^{-1} of detection limit. As regarding the selectivity studies, a lot of compounds were investigated. Two thousand-fold concentration of different cations and anions: K^+, Na^+, Cl^-, Ba^{2+}, Mg^{2+}, Ca^{2+}, Al^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, CH_3COO^-, $NH_4{}^+$, $C_2O_4{}^{2-}$, $NO_3{}^-$, $SO_4{}^{2-}$ showed no change in current peak height for the oxidation of BPA (2.0×10^{-6} mol L^{-1}). An increase in peak current in the presence of more than 50-fold amount of Fe^{3+} and 500-fold amount of Cu^{2+} ion was noticed. Other organic possible interfering species such as glucose (GLU), catechol (CAT), phenol (PHE), 4-aminophenol (4-APH), 2,4-dinitrophenol (2,4-DNP), p-nitrophenol (p-NPH), o-nitrophenol (o-NPH), hydroquinone (HQU) were tested and it can be seen that 50-fold concentration from these compounds have no interference toward determination of 2.0×10^{-6} mol L^{-1} BPA. To assess the reproducibility of



Scheme 2. Schematic diagram of the preparation of anti-BPA/AuNPs/N,S,P-CDs/GCE and electrochemical detection process (Copyright permission from the publisher "The Electrochemical Society").

the method intra-day and inter-day assay have been conducted with an RSD value lower than 5.7%. The results obtained in plastic product samples for the determination of BPA using the proposed sensor were in good agreement with UV-Vis technique, the calculated t-test was 0.035.[29]

Sidwaba and his collaborators reported an electrochemical manganese peroxidase (MnP) biosensor fabricated on a GCE modified with a nanocomposite formed from conducting polyaniline (PANI), polymethyl methacrylate (PMMA), and titanium dioxide (TiO_2) nanoparticles. The calculated limit of detection was 1.7×10^{-10} mol L^{-1}, but a linear concentration range not so wide, from 2.0×10^{-10} mol L^{-1} until 1.2×10^{-9} mol L^{-1}. Higher concentrations of BPA were not discussed in this report, regarding the fact that BPA tends to polymerase and at higher concentrations creates an insulating film on top of the electrode, fact that makes impossible to be determined without preparing a fresh biosensor. Also, the enzyme gets saturated when the concentration of BPA gets higher. The nanocomposite immobilized on top of the GCE presented enhanced electroconductivity of PANI which was attributed to the synergistic effect of the incorporated TiO_2 nanoparticles and PMMA. No interference studies or analytical applications were discussed.[30]

Yao, Liu and Yang reported an electrochemical aptasensor based on AuNPs and nitrogen, sulfur and phosphorus co-doped carbon dots (N, S, P-CDs) modified GCE. The limit of detection was quite low, 5.3×10^{-10} mol L^{-1}. In the first step, the N, S, P-CDs were coated on top of the GCE to increase the active area of the working electrode, then the AuNPs were dripped on top of the modified GCE to obtain the Au-thiol strong bond that favor the immobilization of the anti-BPA aptamer (Scheme 2). The stability of the proposed aptasensor was tested after a period of 3 weeks to observe a less that 10% decrease in signal, and after 8 weeks the signal response was 84.2% of the original signal. The authors discussed the selectivity of the method using a large number of interfering species, such as 10 μmol L^{-1} of Na^+, 10 μmol L^{-1} of K^+, 10 μmol L^{-1} of Cu^{2+}, 10 μmol L^{-1} of Zn^{2+}, 10 μmol L^{-1} of Ca^{2+}, 10 μmol L^{-1} of bisphenol B, 10 μmol L^{-1} phenol, 10 μmol L^{-1} of L-cysteine, 10 μmol L^{-1} of 4,4'-sulfonyldiphenol, 10 μmol L^{-1} of 2,5-diamino-benzenesulfonic acid, 10 μmol L^{-1} sulfanilic acid, 10 μmol L^{-1} of hydroquinone, mixture solution 1 (containing 10 μmol L^{-1} Na^+, K^+, Cu^{2+}, Zn^{2+}, Ca^{2+}, bisphenol B, phenol, L-cysteine, 4, 4'-sulfonyldiphenol, 2, 5-diamino-Benzenesulfonic acid, sulfanilic acid and hydroquinone) and mixture solution 2 (containing 1000 μmol L^{-1} of all the cations and organic compounds from mixture solution 1). No significance influence was observed in the signal obtained for the oxidation of BPA, proving once more that aptasensors are quite selective tools.[31]

Screen-printed electrodes for determination of bisphenol A.— Screen-printed electrodes (SPEs) have become a novel approach for determination of BPA from real samples, due to the miniaturized aspect and ease of surface modification. In Table II, different types of materials used for modifying the surface of SPE for determination of BPA are presented. Using SPEs allows the miniaturizing electrochemical sensors to become portable devices.

In 2010, Brugnera, Goncalves-Trindade and Boldrin-Zanoni used cetyltrimethylammonium bromide surfactant (CTAB) to achieve the anti-fouling effect of the electrode, especially for the determination of BPA. This type of cationic surfactant was used previously, in the construction of a carbon paste electrode for determination of BPA from plastic samples, where the LOD was lower 7.5×10^{-9} mol L^{-1}[32] than 5.1×10^{-8} mol L^{-1} obtained using CTAB-SPE. The proposed method

Table II. Modified screen printed electrodes for the determination of BPA.

Screen printed electrode modified with:	Limit of detection (mol L^{-1})	Samples	Reference
CTAB	5.1×10^{-8} mol L^{-1}	River water and sewage	32
Laccase–thionine–carbon black	2.0×10^{-7} mol L^{-1}	Tomato juice from metallic cans	35
AuNPs-rGO-CNT	8.0×10^{-10} mol L^{-1}	-	36
MIP	6.0×10^{-11} mol L^{-1}	-	37
PEI-PC/DPNs/AuNPs	6.6×10^{-9} mol L^{-1}	Tap water	38
US-MagMIP/CBNPs/AuNPs	8.8×10^{-9} mol L^{-1}	Tap and mineral water	39

was also tested for BPA determination in the presence of nonylphenol (NP), and BPA could be measured in the presence of NP, only when the pH is adjusted to pH 8.0, and NP is in non-anionic form. Using the proposed method, both BPA and NP were able to be determined from sewage samples, and BPA was recovered in percentage higher than 96% from river waters, results which were in good correlation with HPLC-diode array detector (DAD) method.[14]

Portaccio and co-workers were the first to report a laccase biosensor for the determination of BPA. Thionine was used as a mediator to enhance the electrochemical performances of carbon black colloidal material. When mediators are involved in laccase-assisted processes, the electron transfer from the mediator to the enzyme is followed by electron donation from the target molecule to oxidized mediator, which gives rise to the regeneration of the mediator.[33,34] The designed laccase-thionine-carbon black SPE had a sensitivity of 5.0 nA/μmol L^{-1} and the LOD was 2×10^{-7} mol L^{-1}. The intra-electrode repeatability was around the 3% ($n = 5$), higher than the inter-electrode reproducibility which was 5%. The operational stability was of about two weeks.[35]

Wang, Cokeliler and Gunasekaran had modified the surface of a SPE with AuNPs, rGO and CNT, by using a facile and green approach to synthesize rGO-CNT nanocomposite. The addition of AuNPs was done because this type of material presents high chemical stability, good biocompatibility, excellent catalytic ability, and enhanced electrical conductivity. Using the employed SPE two linear ranges were observed, from 1.45×10^{-9} to 2.0×10^{-8} mol L^{-1} and from 2.0×10^{-8} mol L^{-1} to 1.49×10^{-6} mol L^{-1}. The electrode preparation was highly reproducible (3.8% RSD). The oxidation peak value of BPA was unaffected by the addition of 10-fold interferents phenol, p-nitrophenol, pyrocatechol, 2,4-dinitrophenol, and hydroquinone. The limit of detection determined was 0.8×10^{-10} mol L^{-1}.[36]

Ekomo and co-workers introduced for the first time molecularly imprinted polymers in the construction of a SPE for detection of organic pollutant, BPA. To play this sensing role, a redox tracer was incorporated inside the binding cavities of a cross-linked MIP, as a functional monomer during the synthesis step. Ferrocenylmethyl methacrylate was used as a redox tracer. It was associated with 4- vinylpyridine as a co-functional monomer and ethylene glycol dimethacrylate as cross-linker for the recognition of the organic pollutant, BPA. This proposed eMIP/SPE showed high affinity toward BPA compared to carbamazepine and ketoprofen. The limit of detection for this disposable SPE was 6.0×10^{-11} mol L^{-1}, being the lowest reported with a modified SPE. No studies were done in real samples using this proposed MIP/SPE.[37]

In 2018, dendritic platinum nanoparticles (DPNs) with a high surface area were prepared and directly coated on gold nanoparticles deposited on a screen-printed carbon electrode, followed by the deposition of a polyethyleneimine-phosphatidylcholine (PEI-PC) layer. By top-coating the SPE with PEI-PC the interference effect was reduced. BPA oxidation potential appeared at 270 mV (lower potential than others mentioned in literature). This SPE revealed two linear ranges for the BPA detection: 1.0×10^{-8}–1.0×10^{-6} mol L^{-1} and 1.0×10^{-6} mol L^{-1} –3.0×10^{-4} mol L^{-1}, with a LOD of 6.6×10^{-9} mol L^{-1}. Tap water samples were used as real samples, and the proposed SPE showed a recovery range from 94.5% to 103.9%, with RSD 3.06%, 6.77% respectively.[38]

Ultrasound-assisted magnetic molecularly imprinted polymer (US-Mag-MIP) combined to an electrochemical sensor modified with a nanocomposite of carbon black nanoparticles (CBNPs), and gold nanoparticles (AuNPs) for highly selective and sensitive detection of BPA. The US-MagMIPs present low toxicity, good biocompatibility as well as good magnetic properties, making them a new tool for biomedical applications. The proposed method exhibits a high sensitivity for BPA with a LOD of 8.8×10^{-9} mol L^{-1} with a wide linear range from 7.0×10^{-8} mol L^{-1} to 1.0×10^{-5} mol L^{-1}. Moreover, this sensor provides a high selectivity toward various likely interferents, such as: caffeic acid, catechin, hydroquinone and 17-β-

Table III. Modified carbon-paste electrodes for the determination of BPA.

Carbon paste electrode modified with:	Limit of detection (mol L^{-1})	Samples	Reference
CTAB	7.50×10^{-9}	PC and PVC products	32
CoPC	1.0×10^{-8}	PVC mineral water bottle, PVC insulation cable, PC mineral water bottle, food package	42
Thionine-Tyr	1.50×10^{-7}	-	43
β-CD/IL	8.30×10^{-8}	Water samples and plastic products	17
ZnO/CNTs/ILCPE	9.00×10^{-9}	Food samples	44
MMIPs NPs/CTAB	1.00×10^{-7}	Water samples and plastic products	15
Bi_2WO_6 nanoplates	2.0×10^{-8}	Milk samples	45
GO nanosheets/IL	5.50×10^{-8}	Water samples	16
Ordered mesoporous carbon/IL	5.00×10^{-8}	Plastic products	18
CdONPs/ILCPE	1.00×10^{-7}	Food samples	19
Ce-doped ZnO	1.8×10^{-8}	Tap water samples	46
nAg-PVP	2.50×10^{-8}	Water samples	47
Au-rGO paste based 3D-printed platform	3.52×10^{-9}	Saliva samples from children	48

estradiol. The proposed SPE showed 4 weeks stability stored in the fridge and the recovery percentage was obtained in the range of 96.4% to 104.3% indicating that the sensor is adequate for application in water samples.[39]

Carbon paste electrodes for determination of bisphenol A – as tools that diminish the fouling effect.—Since their discovery, in 1958,[40] carbon paste electrodes (CPEs) underwent a remarkable development and they had been used worldwide in many areas, such as biomedical field, environmental field, food industry field and so on.

Covering all these three application fields, CPEs modified with various compounds were used for fast determination of BPA from water samples, plastic samples, and biological samples. The advantages of CPEs are the following: simplistic and cheap design, ease of miniaturization, fast reproducible surface area, small amounts of samples and stock solutions needed. This kind of electrochemical sensors represent an interesting tool for the determination of BPA (see Table III) due to their highly reproducible surface area, which promotes the anti-fouling effect.

In 2005, Huang used a surfactant, cetyltrimethylammonium bromide (CTAB), as modifier in the design of CPE for determination of BPA. The surfactant‘s hydrophobic and hydrophilic groups can change the electrode-solution interaction and influence the electrochemical process.[41] Adsorption of this kind of chemical aggregates on the electrode surface can favor the electron transfer, the change of oxidation potential and also alter the stability of the electrochemical reaction secondary products, diminishing or eliminating the formation of an insulating film (the formation of this film creates the fouling effect) that can block the further electro oxidation of the analyte. CTAB promotes the electron transfer between the BPA solution and CPE and the oxidation peak currents were considerably higher, and the limit of detection quite low (7.5×10^{-9} mol L^{-1}) with RSD value of 5.6%. The proposed sensor showed, in optimal conditions, a very good selectivity toward BPA determination in the presence of the following possible interfering species: Fe^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, Hg^{2+}, $CO_3{}^{2-}$, Cl^-, $NO_3{}^-$, 2,4-dinitrophenol, 2(4)-nitrophenol, phenol, 2-aminophenol and ethanol. The BPA recovery from PC and PVC samples was between 99.4 and 102.6%.[32]

Cobalt-phthalocyanine (Co-PC) was added to a CPE to form a modified CPE for the determination of BPA from plastic products. Co-PC complex is able to catalyze the electrochemical reaction of organic compounds and it becomes an important redox mediator, which has shown great potential for the electrocatalytic analysis of phenolic type chemicals.[44] Co-PC/CPE reached a detection limit of 1.0×10^{-8} mol L^{-1}. In the selectivity studies, phenol, hydroquinone, hydroxyphenol, pyrocatechol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, p-nitroaniline and several cations (100 fold concentration) have no influence on the signals of BPA with deviations below 5%. As real samples different kinds of plastic products were studied: PVC mineral water bottle, PVC insulation cable, polycarbonate mineral water bottle, and food package. The recoveries of BPA from these samples were between 92.1 and 107.8%.[42]

A CPE was modified, in 2010, with thionine as mediator and the enzyme tyrosinase as bioactive element for the determination of BPA. Regarding the stability, the authors declare that no sensor was used if the current response decreased under 7% than the initial one. The intraelectrode repeatability was less than 2% ($n = 5$) while the interelectrode reproducibility was around 7%. The LOD was 1.50×10^{-7} mol L^{-1}. Using the proposed biosensor cathecol and BPA were both determined, but no applications in real samples were studied.[43]

β-cyclodextrin was used as modifier in the design of an IL-CPE for the determination of BPA from water samples and plastic products. The IL, 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIMBF_4$), was used as a conductive binder in the modified paste. β-cyclodextrin as modifier presented highly selectivity toward determination of BPA and enhanced sensitivity, due to lower electron transfer resistance (Ret) value obtained in the EIS measurements. The proposed IL-CPE reached 8.3×10^{-8} mol L^{-1} detection limit. Stability was tested and after 15 days the current response was 90%, and when not in use the proposed CPE was stored at 4°C. 500-fold concentration of inorganic anions and cations had no influence on the signal of BPA with a deviation below 5%. 30-fold concentration for hydroquinone, resorcinol, 2,4-dichlorophenol, and 80-fold for phenol, p-nitrophenol, 2,4-dinitrophenol, 2,4,6-trichlorophenol, respectively were the tolerance limits for determination of BPA in the presence of these organic compounds. The results obtained for the recovery of BPA from tap water, river water, PC water bottle and PVC food package bag were in good correlation with the ones obtained using HPLC method.[32]

The anti-fouling surfactant CTAB was used to design a molecularly imprinted polymer CPE for the determination of BPA from water samples and plastic products. The polymer imprinting favors electron transfer and lowers the Rct value. The deviation of the anodic peak current recorded for 45μmol L^{-1} BPA solution using the same MIP/CTAB/CPE was 1.4% for 7 measurements and 4.3% for 3 newly prepared MIP/CTAB/CPE. The stability was studied for 30 days and the anodic peak current decreased with 8.6% than the initial value. The LOD was quite high, 1.00×10^{-7} mol L^{-1}, than the other CPE discussed in this chapter. Drinking bottles and lake waters were used for the analytical applications and the recovery percentage were between 95% and 112%.[33]

Najafi and co-workers described the synthesis of a new ZnO/CNTs nanocomposite used to modify an ILCPE. The IL used as oily binder was 1,3-dipropylimidazolium bromide. The storage condition for the ZnO/CNTs-ILCPE was in the fridge at 4°C and after 4 weeks, only a small decrease in the peak current of the BPA oxidation was observed. After 10 consecutive scans the proposed sensor showed good reproducibility of the peak current with RSD value of 2.0%. The LOD was 9.00×10^{-9} mol L^{-1}. The tolerance limit for determination of BPA in the presence of possible interfering species was 1000-fold for glucose, sucrose, lactose, fructose, methanol and ethanol, 800-fold for different anions and cations and 700-fold for citric acid and various aminoacids. The food samples tested successfully for BPA levels were tomato paste, corn, stew, tuna fish, and chili sauce.[44]

BPA and diethylstilbestrol was simultaneous determined from milk samples using a Bi_2WO_6 nanoplates modified CPE. Bi_2WO_6 is a semiconductor that enhanced the transfer of electrons to the surface of the electrode. The obtained LOD for BPA determination was 1.0×10^{-8} mol L^{-1}. The reproducibility studies showed a deviation of 4.1% in the current response for analysis of BPA. The proposed CPE retained more than 92% of its initial current response after kept in the fridge for 2 weeks. 100-fold concentration of glucose, anions and cations, 20-fold concentration of hydroquinone, hydroxyphenol, pyrocatechol and phenol and 10-fold concentration of dopamine and ascorbic acid showed no influence on the signals obtained for the oxidation of BPA. Spiked samples of milk were used for analytical application of the proposed method, showing a recovery percentage range from 88% to 98%.[45]

In 2015, a new CPE modified with GO nanosheets and (n-hexyl-3-methylimidazolium hexafluoro-phosphate was constructed for the determination of BPA from water samples. The anti-fouling properties were tested by submitting a BPA solution to repeated CV cycles (15 cycles). The peak potentials were unchanged and the currents decreased by less than 2.43%. The proposed sensor covered a wide concentration range with a limit of detection of 5.5×10^{-9} mol L^{-1}. A long term stability study was performed for a three week period and the current response showed less than 2.6% decrease due to the initial current response. The water samples used for analytical applications were drinking water samples, river water samples and wastewater samples. The recovery percentage was above 96.0%.[16]

As Yu et al.,[17] Li and coworkers replaced the paraffin oil with an ionic liquid, 1-butylpyridinium hexafluorophosphate ($BPPF_6$), as binder for paste electrode preparation, due its high ionic conductivity, high viscosity, providing a fast electron transfer rate and a decrease in the overpotential of BPA. The authors added ordered mesoporous carbon CMK-3 to the nano-carbon paste to display low resistance, high sensitivity, large surface area and adsorption capability of the CMK-3. The diameter of the CMK3/nano-CILPE was

3.0 mm and the calculated limit of detection was 5×10^{-8} mol L^{-1}. The RSD of the response current was 4.6% and the stability of the nano-ILCPE was very good, 95.7% of the initial current response was kept after a month. 500-fold concentration of ions and cations showed peak current changes in the determination of BPA less than 5% and 100-fold concentration of organic compounds similar with BPA showed no interference in the determination of BPA. The recovery of BPA from PC plastic bags and drinking bottles were between 98.9% and 101.8%.[18]

Also, Arabali et al. used an IL, n-hexyl-3-methylimidazolium hexafluoro phosphate, as binder for the CPE and CdO nanoparticles to modify the carbon paste (CdONPs/ILCPE). The RSD% for 10 successive measurements was 1.7%. When using 7 different electrodes, the RSD% for 9 measurements was 2.7%. When the electrode was stored at room temperature, the modified CPE retains 96% of its initial current response after 10 days and 92% after 40 days. The LOD was not that low, 1.0×10^{-7} mol L^{-1}. The tolerance limit for determination of BPA in the presence of possible interfering species was similar with the results obtained by Najafi and co-workers.[49] The difference consists in tolerance limit for cations and anions which was higher, 900-fold concentration. The CdONPs/ILCPE retained its efficiency for the determination of bisphenol A, in food samples, such as tomato paste, corn, stew, tuna fish.[19]

In 2018, Zhou et al. proposed cerium-doped zinc oxide nanorods (Ce-ZnO) modified CPE as selective sensor for the determination of BPA. This is the first time when a rare earth metal (Ce) is used as doping ion in the material of the working electrode used for the determination of BPA. The addition of this rare earth ion enhances the current intensity recorded for the oxidation of BPA. The whole process of the possible catalytic mechanism of the proposed Ce-doped ZnO/CPE is presented in Fig. 3. The limit of detection was 1.8×10^{-8} mol L^{-1}. In order to investigate the selectivity of Ce-doped ZnO/CPE, 100-fold of inorganic ions (Ca^{2+}, Mg^{2+}, $SO_4{}^{2-}$ and NO^{3-} ions), 200-fold of saccharides (glucose, fructose, lactose, sucrose), 300-fold of amino acids (tryptophan, methionine, glycine, isoleucine, histidine, alanine, threonine), 10-fold of plasticizer (dioctyl phthalate) and 5-fold of phenol compounds (pyrocatechol, hydroxyphenol, 4-aminophenol) were used as possible interfering species with no influence in the detection of 50 μmol L^{-1} BPA. The proposed CPE was employed for BPA determination from tap water samples with recovery percentage ranged between 93.3% and 103.3%.[46]

BPA and hydroquinone (HQ) were simultaneous determined using a CPE modified with poly-vinylpyrrolidone Ag nanoparticles (nAg-PVP) The PVP was used as a reducing agent of nAg from $AgNO_3$ in aqueous media. The calculated LOD for BPA was 2.5×10^{-8} mol L^{-1}. The repeatability of the measurements was good, with a RSD value of 1.94% for BPA over a 10-days period and after 30 days of storage the proposed sensor showed a decrease in the current intensity for the oxidation of BPA with 20%. The potential interfering species considered in this paper were glucose, sucrose, uric acid, urea, ascorbic acid, K^+, Na^+, Cl^- and Ca^{2+}. The interferent/BPA ratio tested was 5:1 with deviations in peak current less than 5.8%. The determination of BPA from water samples was done using the proposed nAg-PVP/CPE and UV-Vis spectroscopy, with good correlation between the results obtained with the two methods.[47]

In 2019, a limit of detection of 3.52×10^{-9} mol L^{-1} was obtained with 3D printing platform based on a novel synthesized Au-rGO composite. The proposed paste electrode showed good results for the determination of BPA from children saliva samples. This method was the only one that described a paste electrode with application on biological samples. The repeatability of the current response for oxidation of BPA showed a deviation of 5.6% for five replicates. The selectivity toward oxidation of BPA was proved by testing the possible interfering species: hydroquinone and methylbenzyl phthalate, which presented different oxidation potential. The high levels of BPA obtained in saliva samples were correlated with the high body mass index of the children patients.[48] In Table IV are summarized other types of sensors used for the determination of BPA.

Other types of sensors for determination of bisphenol A.—Yang and collaborators were the first who screened a BPA-specific peptide sequence heptapeptide sequence Cys-Lys-Ser-Leu-Glu-Asn-Ser-Tyr- Cys (CKSLENSYC) in order to develop a peptide-based electrochemical biosensor for BPA detection. Cysteine flanked heptapeptide exhibited a specific affinity toward BPA and was identified through bio panning procedure. The concentration range covered with linear correlation was from $1.0 \times 10^{-9} - 5 \times 10^{-6}$ mol L^{-1}, with a calculated limit of detection of 7.0×10^{-10} mol L^{-1}. To test the reproducibility of the method five electrodes were prepared in the same way and tested for BPA determination and the RSD value was 7.6%. Also, regeneration on the surface of the electrode was proposed, and was able to be employed for up to three times. The storage condition of the biosensor was 4°C in the refrigerator for 30 days. The specific Cys-peptide/Au electrode showed a preferential high selectivity toward BPA with negligible cross-reactivity to Ca^{2+}, phenol, 2,4-dinitrophenol, 2-nitrophenol and 4,4'-dihydroxybiphenyl. Spiked recoveries from plastic products were between 92% and 107%.[49]

Pogacean and co-workers were the first to propose two bimetallic-graphene composites to modify a Au electrode for voltammetric determination of BPA. Preparation of graphene decorated with bimetallic nanoparticles (AuCu and AgCu) showed and enhance electro-catalytic response. AgCu nanoparticles covered a higher graphene are and the size of nanoparticles was between 20–50nm, while the AuCu nanoparticles were smaller 10–25nm but covered a smaller graphene area. Considering this, during electrochemical studies the sensor based on AgCu-graphene had a larger calculated active area, lower detection limit and higher sensitivity, than the other graphene bimetallic nanocomposite modified Au electrode. Cathecol and 3-nitrophenol were tested for interferences in the oxidation of BPA using the porposed two sensors, showing no interfering effect, proving the selectivity toward the determination of BPA. No real samples were analyzed in this study.[50]

Three modified pencil graphite electrodes (PGE) were reported in the literature for the determination of BPA from various wa-

Table IV. Different types of modified electrodes for the determination of BPA.

Electrode based on	Limit of detection	Samples	Reference
CKSLENSYC-Au	7.0×10^{-10} mol L^{-1}	Plastic products	49
Gr-AgCu/Au electrode	1.3×10^{-6} mol L^{-1}	-	50
Gr-AuCu/Au electrode	1.9×10^{-6} mol L^{-1}		
Polyaniline-MWCNT/PGE	1.0×10^{-1} mol L^{-1}	Baby bottle water	51
ETPGE-PGE	3.1×10^{-9} mol L^{-1}	River water samples	52
AuNP/PVP/PGE	1.0×10^{-9} mol L^{-1}	Bottled drinking water	53
f-MWCNTs/AuNPs/ Au electrode	5.0×10^{-11} mol L^{-1}	Mineral water Orange juice Milk samples	54
Aptamer-MCH-AuNPs-BDD	7.2×10^{-15} mol L^{-1}	Milk samples	20
MB-ssDNAaptamer/AuPET	1.75×10^{-12} mol L^{-1}	tap water, PC plastic bottle, PVC plastic toy	56

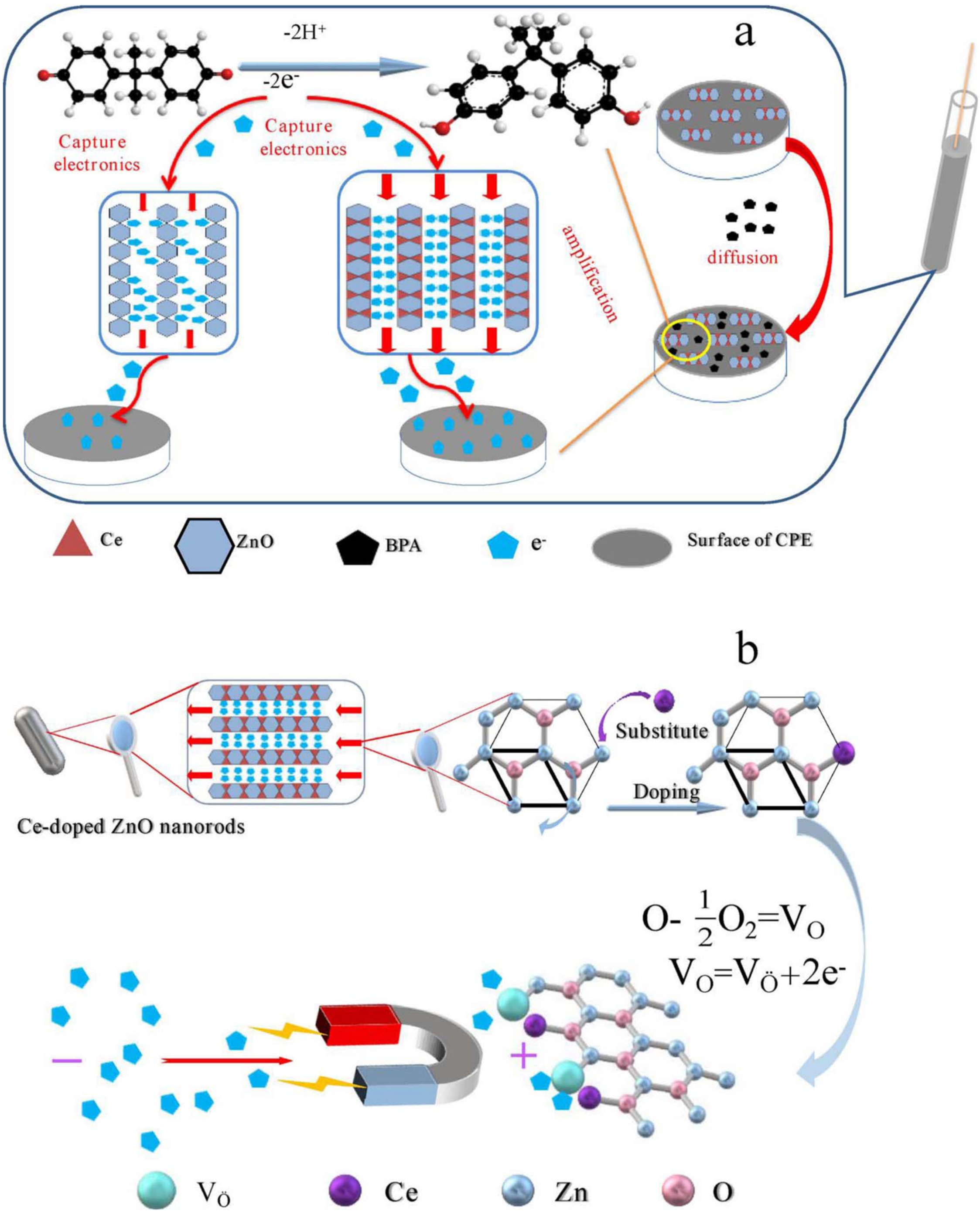


Figure 3. (a) Possible catalytic mechanism of the proposed Ce-doped ZnO/CPE. (b) The speculated electron capturing process occurred on Ce-doped ZnO nanorods. (Copyright permission from the publisher "The Electrochemical Society").

ter samples.[51–53] In 2011, Poorahong and co-workers proposed polyaniline nanorods (PANI) and multiwalled carbon nanotubes (MWCNTs) for the modification of PGE, obtaining 1.0×10^{-8} mol L^{-1} LOD.[51] In 2014, Ozcan electrochemically treated (ET) for the first time a PGE with $LiClO_4$ and NaOH, to obtain a ETPGE for determination of BPA from water samples. This electrochemical treatment with different supporting electrolytes enhances the selectivity toward a molecule. The proposed ETPGE reached a lower LOD 3.1×10^{-9} mol L^{-1}, than the PGE reported above, and from seven organic molecules, similar in structure with BPA, only phenol showed a slightly interference.[52] In 2016, Yaman and Abaci combined AuNPs with the polymer polyvinylpyrrolidone (PVP), to modify the surface of a PGE for determination of BPA from bottled drinking water. The LOD obtained was the lowest from all three PGE, 1.0×10^{-9} mol L^{-1}. The interference effects of 50-fold concentration of 2,4-Dinitrophenol, p-Nitrophenol, o-Nitrophenol and 200-fold concentration of different cations were examined and had no influence in the oxidation of BPA with the AuNPs-PVP/PGE. The proposed process was successfully applied to define BPA in bottled drinking water with high reliability and recovery range from 93% to 103%.[53]

A functionalized-multiwall carbon nanotubes/gold nanoparticles (f-MWCNTs/AuNPs) nanocomposite film modified gold electrode was described for determination of BPA from mineral water, orange juice and milk samples. Both MWCNTs/AuNPs exhibited an increase in the conductivity of the electrode. The LOD was low, 5.0×10^{-11} mol L^{-1} and the analytical application of the proposed sensors were done by measuring the BPA level from mineral water, orange juice, milk samples.[54]

Ma and coworkers reported in 2017 a modified boron-doped diamond (BDD) electrode with Au nanoparticles (Au-NPs), aptamers, and 6-mercapto-1-hexanol (MCH). Femtomolar detection limit of 7.2×10^{-15} mol L^{-1} was achieved. Boron-doped diamond (BDD) has been proposed as electrode material due to its unique characters such as chemical inertness, wide potential window in aqueous solutions, very low background current, electrostatic capacity, high current density, excellent electrochemical stability, and high resistance to fouling.[55] The structure of aptamer was 5′-SH-(CH2)6-CCG GTG GGT GGT CAG GTG GGA TAG CGT TCC GCG TAT GGC CCA GCG CAT CAC GGG TTC GCA CCA-3′. The gold nanoparticles present high affinity for the thiol groups, and that is why the aptamer binding on top on the AuNPs/BDD is very stable.[20]

In 2019, Yu and coworkers proposed a disposable aptasensor based on methylen blue (MB)-aptamer-Au modified polyethylene terephthalate electrode (Au/PET electrode) for the determination of picolevels of BPA from plastic products and water samples. The aptamer sequence was 5′-CCG GTG GGT GGT CAG GTG GGA TAG CGT TCC GCG TAT GGC CCA GCG CAT CAC GGG TTC GCA CCA-3′. The LOD obtained was 1.75×10^{-12} mol L^{-1}, with RSD value between 3.1% and 12.3%, showing acceptable reproducibility of the aptasensor. Possible interference from seven chemicals with similar structure to BPA, including phenol (PN), 4-nitrophenpl (NPN), hydroquinone (HQ), 4,4’-bisphenol (BP), bisphenol B (BPB), and 6F-bisphenol (6F-BPA), were examined and the specific interaction between the aptamer and BPA was confirmed. Real samples used in this study were tap water, PC plastic bottle and PVC plastic toy. In these samples, the detectable BPA was only found in the PVC plastic toy.[56]

Conclusions

In conclusion, various electrochemical sensors have been developed for the detection of BPA in a variety of samples, because it is a worldwide need to be able to use a fast method to determine the BPA levels from plastic household items, food, water or biological samples.

The modification of electrochemical sensors showed great enhancement of current response for electro-oxidation of BPA, antifouling effect, high sensitivity, selectivity and stability.

Mainly three types of electrochemical sensors have been reviewed in this paper: modified glassy-carbon electrodes; modified screen-printed electrodes and modified carbon paste electrodes. The modification with gold nanoparticles showed the most increased conductivity of the electrode, while the aptamer modification of the electrode showed the highest selectivity and sensitivity, and low detection limits. But while the aptasensors are not that stable and need low temperature storage conditions, the other types of sensors showed a greater stability in time. While glassy carbon electrodes are the most used substrate for modification, they are also bigger in diameter, while screen printed and paste electrode are miniaturized tools and the amount of samples used is very small. Carbon paste electrodes are the cheapest and present easy ways of preparations. They also exhibit the possibility to fast renew the active surface area, being able to eliminate the fouling effect. It is well known that in the preparation of a CPE, an oily binder is used to create the paste. This mineral oil is an insulating material, and maybe the reason why some types the recorded current range in lower than when using SPE or GCE. This overcome this problem, ionic liquids where used as binder material to form the CPE, due to the fact that ILs present high conductivity and high viscosity.

The choice of electrochemical sensor for the determination of BPA should also be influenced by the type of real samples that are used in applications. Some of the applications need low detection limits, some need wide concentration range, and some need extremely selective and stable method, while other applications need to cover a concentration range higher than μmolar levels of BPA.

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References

1. E. Ribeiro, C. Ladeira, and S. Viegas, *Toxics*, **5**, 22 (2017).
2. T. Watanabe, H. Yamamoto, K. Inoue, A. Yamaguchi, Y. Yoshimura, K. Kato, H. Nakazawa, N. Kuroda, and K. Nakashima, *J. Chromatogr. B*, **762**, 1 (2001).
3. K. Ouchi and S. Watanabe, *J. Chromatogr. B*, **780**, 365 (2002).
4. Y. Sun, M. Irie, N. Kishikawa, M. Wada, N. Kuroda, and K. Nakashima, *Biomed. Chromatogr.*, **18**, 501 (2004).
5. Y. Lei, L. Fang, M. S. H. Akash, Z. Liu, W. Shi, and S. Chen, *Anal. Meth.*, **5**, 6106 (2013).
6. Y. Zhu, C. Zhou, X. Yan, Y. Yan, and Q. Wang, *Anal. Chim Acta*, **883**, 81 (2015).
7. Z. Zheng, J. Liu, M. Wang, J. Cao, L. Li, C. Wang, and N. Feng, *J. Electrochem. Soc.*, **163**, B192 (2016).
8. Y. Xu, W. Lei, Y. Zhang, H. Fan, Q. Hao, and S. Gao, *J. Electrochem. Soc.*, **164**, B3043 (2017).
9. G. Zhu, J. Qian, H. Sun, Y. Yi, and X. Wu, *J. Electrochem. Soc.*, **164**, H545 (2017).
10. R. I. Stefan-van Staden, A. Moscalu-Lungu, and J. F. van Staden, *J. Electrochem. Soc.*, **166**, B903 (2019).
11. J. Zhao, Y. Ma, X. Hou, L. Li, P. Zheng, and C. Li, *J. Solid State Electrochem.*, **19**, 1571 (2015).
12. H. Yin, L. Cui, S. Ai, H. Fan, and L. Zhu, *Electrochim. Acta*, **55**, 603 (2010).
13. X. Wang, J. Chen, M. Wu, Y. Shi, M. Li, J. Shan, and L. Liu, *J. Electrochem. Soc.*, **165**, B814 (2018).
14. M. F. Brugnera, M. A. Goncalves-Trindade, and V. Boldrin-Zanoni, *Anal. Lett.*, **43**, 2823 (2010).
15. L. Zhu, Y. Cao, and G. Cao, *Biosens. Bioelectron.*, **54**, 21 (2014).
16. H. Beitollahi and S. Tajik, *Environ. Monit. Assess.*, **187**, 257 (2015).
17. X. W. Yu, Y. K. Chen, L. P. Chang, L. Zhao, F. X. Tang, and X. P. Wu, *Sens. Actuator. B*, 186, **648**, (2013).
18. Y. Li, X. Zhai, X. Liu, L. Wang, H. Liu, and H. Wang, *Talanta*, **148**, 362 (2016).
19. V. Arabali, M. Ebrahimi, S. Gheibi, F. Khaleghi, M. Bijad, A. Rudbaraki, M. Abbasghorbani, and M. R. Ganjali, *Food Anal. Meth.*, **9**, 1763 (2016).
20. Y. Ma, J. Liu, and H. Li, *Biosens and Bioelectron*, **92**, 21 (2017).
21. H. Yin, L. Cui, S. Ai, H. Fan, and L. Zhu, *Electrochim. Acta*, **55**, 603 (2010).
22. H. Fan, Y. Li, D. Wu, H. Ma, K. Mai, D. Fan, B. Du, H. Li, and Q. Wei, *Anal. Chim. Acta*, **711**, 24 (2012).
23. Y. Qu, M. Ma, Z. Wang, G. Zhan, B. Li, X. Wang, H. Fang, H. Zhang, and C. Li, *Biosens and Bioelectron*, **44**, 85 (2013).
24. N. Huang, M. Liu, H. Li, Y. Zhang, and S. Yao, *Anal. Chim. Acta*, **853**, 249 (2015).
25. D. Pan, Y. Gu, H. Lan, Y. Sun, and H. Gao, *Anal. Chim. Acta*, **853**, 297 (2015).
26. L. Wu, H. Yan, J. Wang, G. Liu, and W. Xie, *J. Electrochem. Soc.*, **16**, B562 (2019).
27. Y. Zhu, C. Zhou, X. Yan, Y. Yan, and Wang Q, *Anal. Chim. Acta*, **883**, 81 (2015).
28. R. Shi, J. Liang, Z. Zhao, A. Liu, and Y. Tian, *Talanta*, **169**, 37 (2017).
29. S. U. Karabiberoglu, *Electroanalysis*, **31**, 91 (2019).
30. U. Sidwaba, N. Ntshongontshi, U. Feleni, L. Wilson, T. Waryo, and E. I. Iwuoha, *Electrocatalysis*, **10**, 323 (2019).
31. J. Yao, C. Liu, and M. Yang, *J. Electrochem. Soc.*, **166**, B1161 (2019).
32. W. Huang, *Bull. Korean Chem. Soc.*, **26**, 1560 (2005).
33. H. P. Call and I. Mucke, *J. Biotechnol.*, **53**, 163 (1997).
34. C. L. Chen, A. Potthast, T. Rosenau, J. S. Gratzl, A. G. Kirkman, D. Nagai, and T. Miyakoshi, *J. Mol. Catal. B:Enzym.*, **8**, 213 (2000).
35. M. Portaccio, D. Di Tuoroa, F. Arduini, D. Moscone, M. Cammarota, D. G. Mita, and M. Leporea, *Electrochim. Acta*, **109**, 340 (2013).
36. Y. C. Wang, D. Cokeliler, and S. Gunasekaran, *Electroanalysis*, **27**, 2527 (2015).
37. V. M. Ekomo, C Branger, R. Bikanga, A. M Florea, G. Istamboulie, C. Calas-Blanchard, T. Noguer, A. Sarbu, and H. Brisset, *Biosens. Bioelectron*, **112**, 156 (2018).
38. K. Shim, J. Kim, M. Shahabuddin, Y. Yamauchi, M. S. A Hossain, and J. H. Kim, *Sens. Actuator. B*, **255**, 2800 (2018).
39. N. B. Messaoud, A. A.Lahcen, C. Dridi, and Z. Amine, *Sens. Actuator. B*, **276**, 304 (2018).
40. R. N. Adams, *Anal. Chem.*, **30**, 1576 (1958).
41. M. Plasvic, D. Krznaric, and B. Cosovic, *Electroanalysis*, **6**, 469 (1994).
42. N. Grootboom and T. Nyokong, *Anal. Chim. Acta*, **432**, 49 (2001).
43. M. Portaccio, A. Di Tuoro, F. Arduini, M. Lepore, D. G. Mita, N Diano, L. Mita, and D. Moscone, *Biosens. Bioelectron.*, **25**, 2003 (2010).
44. M. Najafi, M. A. Khalilzadeh, and H. Karimi-Maleh, *Food Chem.*, **158**, 125 (2014).
45. L. Peng, S. Dong, H. Xie, G. Gu, Z. He, J. Lu, and T. Huang, *J. Electroanal. Chem.*, **726**, 15 (2014).
46. Y. Zhao, C. Hao, Y. Dang, and S. Chen, *J. Electrochem. Soc.*, **165**, H962 (2018).
47. F. Ianesko, C. Alves de Lima, C. Antoniazzi, E. R. Santana, J. V. Piovesan, A. Spinelli, A. Galli, and E. Guimaraes de Castro, *Electroanalysis*, **30**, 1946 (2018).

48. L. A. Gugoasa, R. I. Stefan-van Staden, J. F. van Staden, M. Coros, and S. Pruneanu, *Anal. Lett.*, **52**, 2583 (2019).
49. J. Yang, S. E. Kim, M. Chao, I. K. Yoo, W. S. Choe, and Y. Lee, *Biosens and Bioelectron*, **61**, 38 (2014).
50. F. Pogacean, A. R. Biris, C. Socaci, M. Coros, L. Magerusan, M. C. Rosu, M. D. Lazar, G. Borodi, and S. Pruneanu, *Nanotechnology*, **27**, 484001 (2016).
51. S. Poorahong, C. Thammakhet, P. Thavarungkul, W. Limbut, A. Numnuam, and P. Kanatharana, *Microchim. Acta*, **176**, 91 (2011).
52. A. Ozcan, *Electroanalysis*, **26**, 1631 (2014).
53. Y. T. Yaman and S. Abaci, *Sensors*, **16**, 756 (2016).
54. B. Deiminiat, G. H. Rounaghi, M. H Arbab-Zavar, and I. Razavipanah, *Sens. Actuator. B.*, **242**, 158 (2017).
55. J. M. Freitas, T. de Costa Oliviera, R. A. Abarza Munoz, and E. M. Richter, *Front Chem*, **7**, 190 (2019).
56. Z. Yu, Y. Luan, H. Li, W. Wang, X. Wang, and Q. Zhang., *Sens. Actuator. B.*, **284**, 73 (2019).