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Novel Sensor Based on Nanocarbon Transducer Functionalized by Iron (III) Porphyrin for the Impedimetric Detection of Bisphenol A

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Abstract

In this chapter, an impedimetric response of iron (III) porphyrin ($\text{Fe}^{(\text{III})}\text{TMPP}$) functionalized on gold transducer towards the detection of three phenolic compounds entitled bisphenol A (BPA), 2,2'-biphenol and catechol has been studied. The bisphenol A that has revealed the best affinity with $\text{Fe}^{(\text{III})}\text{TMPP}$ membrane has been chosen as the target analyte. For improved sensitivity of $\text{Au}/\text{Fe}^{(\text{III})}\text{TMPP}$ sensor towards BPA, a facile and efficient Au/RGO nanocarbon transducer based on reduced graphene oxide (RGO) has been prepared and used to support $\text{Fe}^{(\text{III})}\text{TMPP}$ membrane. The obtained $\text{Au}/\text{RGO}/\text{Fe}^{(\text{III})}\text{TMPP}$ structure was characterized by UV-visible (UV-vis) and electrochemical impedance spectroscopy (EIS) measurements, then applied as electrochemical platform for BPA detection. It has been discovered that the Au/RGO nanocarbon transducer has an amplified electron transfer kinetic compared to unmodified Au transducer. The $\text{Au}/\text{RGO}/\text{Fe}^{(\text{III})}\text{TMPP}$ structure has showed a better affinity towards BPA with a doubled sensitivity compared to that obtained with $\text{Au}/\text{Fe}^{(\text{III})}\text{TMPP}$ electrode. We demonstrated that the Au/RGO nanocarbon transducer not only enhances the electron transfer ability but also serves as a good template for the attachment of $\text{Fe}^{(\text{III})}\text{TMPP}$ through π - π interaction. This study reveals new high-potential of nanocarbon transducer based on RGO for the conception of electrochemical sensors with high sensitivity and short response time.

Keywords: iron (III) porphyrin, reduced graphene oxide, impedimetric sensor, nanocarbon transducer, bisphenol A

1. Introduction

Bisphenol A (BPA, 2, 2-bis (4-hydroxy phenyl) propane), is one of the most extensively used industrial compounds in the production of plastics due to its transparent, strong and light characteristics [1]. Till now, BPA has been widely employed as a monomer to synthesize polycarbonate, epoxy resin, polysulfone resin and other various polymer materials [2]. These polymer materials are mostly used to produce storage containers, nursing bottles, thermal papers, medical apparatus, food can linings and supply pipes [3]. However, toxicology studies have

shown that BPA is a typical endocrine-disrupting compound (EDC) in which even a low level can mimic and interfere with hormonal activity by interfering with growth and reproductive development [4, 5]. Consequently, the popular use of BPA has raised serious concerns regarding its implications for food safety and environmental health. In fact, BPA can be released from waste plastics, thermal printing papers, compact disks, powder paints, and adhesives into food and water samples at low concentration (ppb level) and will eventually find its way into the human body [6]. Unsurprisingly, BPA was found to be present in many biological fluids such as human blood, serum, and urine [1]. Although many countries have begun to phase out the use of BPA [7], several of the BPA-containing products that often occupy landfills are still around. This means that BPA will continue to migrate into the environment through runoff and wastewater discharges, eventually contaminating our water resources and food supplies. Therefore, it is still needed to develop a sensitive and simple method for the determination of trace amounts of BPA in the environment. Notably, multiple procedures have been utilized for determining the contents of BPA in diverse matrices, including liquid chromatography-mass spectrometry [8], electrochemiluminescence, colorimetry, liquid chromatography coupled to UV/vis, fluorescence spectrometry, enzyme-linked immunosorbent assay (ELISA) [9], surface-enhanced Raman scattering (SERS) [10] and so forth. These methods can offer good accuracy and sensitivity, however they have some drawbacks, such as high-cost equipment, time consuming operation and unsuitability for onsite analysis [11, 12], thus restricting their application. On contrary, electrochemical sensors have been extensively used as an alternative solution for detecting trace levels of BPA due to their inherent advantages such as low cost, short analysis time, portability and excellent sensitivity [13]. Direct monitor BPA using an electrochemical sensor with a bare electrode has a poor response due to fouling and sluggish electron transfer kinetics [14]. In order to avoid and reduce this problem, several kinds of nanomaterials or their composites with excellent catalytic properties have been employed to modify the electrode. Amongst such materials, porphyrins and their derivatives have been long employed in electrochemical sensors applications [15] thanks to their special electrochemical properties [16]. These latter originated from the highly π -conjugated system of porphyrin which is an efficient platform for electron transfer [17]. Indeed, porphyrins are naturally occurring macrocyclic species that bind metals *via* nitrogen donor atoms on four pyrrole subunits, resulting in versatile chelating systems [18]. The coordination sites of porphyrin molecule can easily connected with metal ions such as Fe, Zn, Mg and so on to form stable metallo-porphyrins. This coordination increases the movement capacity of electrons [19], thus the electrocatalytic activity of the porphyrin. Among the metalloporphyrins, iron porphyrins have demonstrated excellent electrocatalysis for many biologically important target molecules [20] thanks to their electronic media role based on their reversible Fe(III)/Fe(II) redox states [21, 22]. Various carbon nanomaterials such as graphene and its derivates have been proven to be excellent carriers to enhance the sensitivity of sensors [23]. Graphene (or reduced graphene oxide, RGO), a 2D material with a single layer of an sp^2 carbon atom network densely packed in a honeycomb structure, has unique properties, such as large surface-to-volume ratio, high adsorption capacity, excellent conductivity and easiness of modifications [24]. This innovative nanocarbon material has been inserted into the sensitive membrane to form a nanocomposite as well as into the transducer to form a nanocarbon transducer. Recently, Nanocarbon Transducers based on RGO have enhanced the target analyte current response which makes them attractive for preparing highly sensitive sensors [25]. The aim of this chapter is to study the effect of nanocarbon transducer on the sensitivity of BPA sensor based on iron (III) porphyrin as a sensitive membrane.

2. Experimental procedure

2.1 Reagents

The triflate iron porphyrin ($\text{Fe}^{(\text{III})}\text{TMPP}$) has been synthesized and characterized by proton NMR and FTIR according to the previously reported procedure [26]. The reduced graphene oxide (RGO) has been synthesized and characterized by FTIR and XPS as described previously [27]. Carbon nanotubes (MWCNTs) used in this study, have been obtained commercially from Baytubes, and produced in a high-yield catalytic process based on chemical vapor deposition (CVD). The diameter of these MWCNTs varies between 5 and 20 nm with a length of over 1 mm. Gold transducer (bare Au), indium tin oxide (ITO), phosphate-buffered saline tablets (PBS, pH = 7.4), acetone ($\geq 99.5\%$), dimethylformamide (DMF, 99.8%), ethanol ($\geq 99.9\%$), bisphenol A (BPA, $\geq 99\%$), catechol ($\geq 99\%$) and 2,2'-biphenol (99%) were purchased from Sigma Aldrich (France).

2.2 Instruments and characterization methods

Electrochemical measurements were performed using an AUTOLAB PGSTAT 100 (supported by "FRA 4.9" software (Methrom)) coupled to a computer and an electrochemical cell (**Figure 1**). The electrochemical measurements were carried out in an electrochemical cell involving a three electrodes system purchased from BASi: bare Au (surface $2.01 \times 10^{-2} \text{ cm}^2$) or modified Au with $\text{Fe}^{(\text{III})}\text{TMPP}$ or RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ membranes as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode and platinum wire as the counter electrode. The analyses were performed by electrochemical impedance spectroscopy (EIS). The modified Au transducer is normally placed in a 0.1 M phosphate buffer solution (PBS (0.1 M), pH = 7) containing target species such as bisphenol A, 2,2'-biphenol and catechol

Figure 1.
Experimental electrochemical measurement device composed by electrochemical cell (place of electrochemical reactions between analytes and the sensitive membrane), potentiostat (electrochemical analysis system) and computer (electrochemical response display).

and then simply followed by fixing the potential. All experiments were conducted at ambient temperature (25°C).

EIS was measured at -0.9 V using an alternating potential of 10 mV amplitude in the frequency range from 100 kHz to 30 mHz.

The UV-vis spectra have been recorded with a Win ASPECT PLUS (validation for SPECORD PLUS version 4.2) spectrometer using a 100 μ l quartz cell.

2.3 Preparation and measurement of electrochemical sensor

The used gold electrodes in this work have a dimension of $1\text{ cm} \times 1\text{ cm}$, where the thickness of the gold deposited by evaporation on Si/SiO₂ substrates is of the order of 50 nm [28]. Before the analysis, in order to improve the adhesion of the sensitive membrane on the electrode surface, the gold substrates were cleaned with acetone in an ultrasonic bath for 10 min and dried under nitrogen flow. Then, the gold substrate has been cleaned in piranha solution ($1/3\text{ H}_2\text{O}_2 + 2/3\text{ H}_2\text{SO}_4$) for about 2 min to activate the surface [29], after this treatment, the gold substrates were rinsed with ultra-pure water and dried under nitrogen flow.

For the preparation of Au/Fe^(III)TMPP sensor, the pretreated gold was drop-casted by 20 μ L of Fe^(III)TMPP solution (4.7 mg in 500 μ l DMF) and dried at 80°C in an oven for 1 h to evaporate residual solvent. The obtained modified electrode was then rinsed with distilled water to remove the non- attached Fe^(III)TMPP and dried under nitrogen flow.

The nanocomposites 2%CNTs/Fe^(III)TMPP and 4%CNTs/Fe^(III)TMPP were prepared by mixing 4.7 mg of Fe^(III)TMPP and different weight proportions of CNTs (2% and 4%) in 500 μ l of DMF followed by sonication in an ultrasonic bath for 2 hours. Then, 20 μ l of each nanocomposite solution was dropped onto the Au electrode, dried at 80°C in an oven for 1 h and rinsed with distilled water prior to electrochemical measurements.

For the construction of Au/RGO/Fe^(III)TMPP sensor, the preparation was divided into two steps. In the first step, the pretreated gold was drop-casted by 20 μ L of RGO solution (1 mg in 1 ml DMF) and dried at 80°C in an oven for 1 h. The obtained Au/RGO nanocarbon transducer electrode was rinsed with distilled water to remove the non-adsorbed materials. In the second step, 20 μ l of Fe^(III)TMPP solution was deposited onto the Au/RGO electrode by drop-casted method. After being dried and washed, the Au/RGO/Fe^(III)TMPP modified electrode was ready to be used for electrochemical measurements.

ITO/Fe^(III)TMPP and ITO/RGO/Fe^(III)TMPP electrodes were prepared using the same procedure for Au/Fe^(III)TMPP and Au/RGO/Fe^(III)TMPP sensors preparations respectively.

3. BPA sensor based on usual transducer functionalized by Fe^(III)TMPP

In order to check the attachment of the Fe^(III)TMPP on the bare Au electrode, electrochemical impedance spectroscopy (EIS) has been selected as a method of characterization thanks to the interfacial charge transfer properties that it can provide for the electrode surface during the modification process [30, 31].

Usually for EIS studies, the first step is to optimize the polarization potential by reducing the warburg diffusion component at low frequencies, which facilitates the interpretation of physico-chemical phenomena [32]. For our study, different negative potentials ($E = -0.6\text{ V}$, -0.7 V , -0.8 V and -0.9 V) have been applied in a large frequency range (100 kHz to 30 mHz). We observe in **Figure 2** an obvious decrease of the half circle diameter correlated with the decrease of the applied

Figure 2.
Optimization of the polarization potential of Au/Fe^(III)TMPP electrode within a frequency range from 100 kHz to 30 mHz and an amplitude of 10 mV sinusoidal modulation in 0.1 M PBS (pH = 7).

potential. This decrease can be explained by the reduction of the charge transfer resistance as a function of the *dc* potential [33], which makes possible the observation of the kinetics of cations at the membrane/solution interface. As a result, we have chosen a continuous polarization of −900 mV throughout our next measurements.

Figure 3 shows the recorded Nyquist plots for bare Au before and after its modification by Fe^(III)TMPP membrane in a PBS solution without any additional external redox probe. The semicircle diameter is related to the charge transfer resistance (R_{ct}) of the electronic transfer from the porphyrin to the electrode [34]. Upon the modification of the Au transducer using Fe^(III)TMPP membrane, the semicircle diameter increased, which means the increase of R_{ct} . This is indicative of a better Au electrode surface coverage with Fe^(III)TMPP accompanied by the decrease in the electronic charge transfer.

The Nyquist diagram of Au/Fe^(III)TMPP electrode can be modeled by an equivalent electrical circuit formed by electrical components. This modeling is done thanks to a software “FRA2” which makes it possible to draw the proposed equivalent electrical circuit optimized by iteration. The choice of the latter is made according to the best fit which corresponds to the lowest value of the total error χ^2 as well as the error on each parameter. The values of the electrical components given for each Nyquist plot illustrate the electronic properties between the transducer/membrane/electrolyte interfaces which facilitate the interpretation of the electronic phenomena during the modification process.

In this study, the choice of the equivalent electric circuit was chosen based on the shape of the Nyquist diagram of the Au/Fe^(III)TMPP electrode as well as on its corresponding bode diagram (**Figure 4**). As can be seen in **Figure 4A**, the total impedance plot of the Au/Fe^(III)TMPP electrode has an enlarged shape. Consequently the Nyquist diagram of the modified electrode can be considered as an

Figure 3. Nyquist plots of bare Au and Au/Fe^(III)TMPP in PBS (0.1 M PBS, pH = 7).

Figure 4. (A) Nyquist and (B) Bode plots of the Au/Fe^(III)TMPP electrode with the fit result.

overlap of two closely interacting semicircles [35] which can indicate the presence of more than one dipole in the equivalent electrical circuit model [36]. **Figure 4B** shows the bode diagram fit of Au/Fe^(III)TMPP electrode. This figure reveals that phase plot presents one phase pic maxima. Consequently, the equivalent electric circuit is analyzed as one dipole [36]. Taking into account the interpretation of Nyquist and bode diagrams of Au/Fe^(III)TMPP, the best circuit that has been chosen is shown in **Figure 5**. This circuit has shown the best fit with low total error χ^2 . This circuit consists of an electrolyte resistance denoted R_s placed in series with one electrical dipole which divides itself into two dipoles. The first dipole is formed by (R_m , CPE1) corresponding to the first high frequency loop and describes the

Figure 5.
 Equivalent circuit used to fit the impedance spectra of Au/Fe^(III)TMPP electrode.

electrochemical phenomena occurring at the electrolyte/membrane interface where R_m is the resistance of the membrane and CPE1 is called the constant phase element. The second dipole is made up by (R_{ct} , CPE2) describing the second loop at low frequencies and describes the electrochemical phenomena occurring at the membrane/electrode interface where R_{ct} represents the charge transfer resistance at the membrane/electrode interface.

In our previous optical study, Fe^(III)TMPP was able to detect BPA molecules through the strong coordination ability of Fe^(III) cation to oxygen atoms [26]. Thus, in this study, the Au/Fe^(III)TMPP electrode has been used to test its ability towards the impedimetric detection of BPA and 2 other interferent molecules. These interfering molecules are 2,2'-biphenol and catechol, which have a structure similar to BPA. The choice of EIS technique to detect these phenolic compounds was made because of its several advantages, such as simplicity, label-free, high sensitivity, and serving as a way to interface recognition events and signal transduction.

BPA is an electron-rich system favorable for the strong interaction with porphyrin ring. Hence, we explore the use of the electrostatic interaction between BPA and cell porphyrin membrane without using any external redox indicator. Thus the detection is directly proportional to the change in the electrical properties of the electroactive Fe^(III)TMPP membrane. **Figure 6** shows the Nyquist plot of Au/Fe^(III)TMPP for different BPA, 2,2'-biphenol and catechol concentrations (from 10^{-12} to 10^{-7} M). Au/Fe^(III)TMPP electrode shows a large increase in diameter of the semicircle, after BPA, 2,2'-biphenol and catechol attachment, correlated with their increasing concentrations, indicating much higher R_{ct} values. This increase can be associated with the multilayer adsorption of BPA, 2,2'-biphenol and catechol molecules on the surface of Fe^(III)TMPP membrane, which leads to the modification of electrochemical properties at the interface.

To confirm this mechanism of detection, the electrochemical proprieties of the sensor have been quantified by fitting the Nyquist plots using the equivalent circuit shown in **Figure 5**. The different fits are done with a total error value (χ^2) less than 10^{-3} . **Figure 7** shows the variation of the membrane resistance R_m as a function of the BPA, 2,2'-biphenol and catechol concentrations cologarithm $p[X] = -\log[CX]$, where X = BPA, 2,2'-biphenol and catechol. We can observe that the value of R_m increases when increasing the concentration of the three studied analytes.

Figure 6.

Nyquist diagrams of Au/Fe^(III)TMPP electrode for different (A) BPA, (B) 2,2'-biphenol and (C) catechol concentrations in PBS (0.1 M, pH = 7). Frequency range [100 kHz–30 mHz]. Potential polarization $E = -900$ mV. The points presenting the experimental data and the line is the fit obtained with the equivalent circuit shown below.

This result indicates an increase in the thickness of the Fe^(III)TMPP membrane, which is proportional to R_m according to the following Eq. (1).

$$R_m = \frac{d}{\delta S} \quad (1)$$

Where d is the membrane thickness, δ is the conductivity of the membrane and S the active area.

Consequently, the increase of the thickness of the Fe^(III)TMPP membrane correlated with the increase of BPA, 2,2'-biphenol and catechol concentrations proves the adsorption of these molecules on the surface of the Fe^(III)TMPP membrane through their π electron system [37].

To fully understand the charge transfer kinetics at the interfaces, the R_{ct} values after BPA, 2,2'-biphenol and catechol attachment were obtained from the equivalent circuit model and used to generate **Figure 8**. This figure describes the evolution of the charge transfer resistance R_{ct} characteristic of the Au/Fe^(III)TMPP interface, as a function of the logarithm of the concentration of BPA, 2,2'-biphenol and catechol. We report, from the curve of $R_{ct} = f(p[X])$, that the charge transfer resistance increased with the increase of BPA, 2,2'-biphenol and catechol concentrations leading to down the electron transfer to Au/Fe^(III)TMPP electrode. This is due to the steric hindrance favored by the multi layers adsorption of the target molecules, which seems logical since it has been shown from Eq. (1) that the sensitive membrane thickness has already increased upon the increasing of the analyte concentrations.

Figure 7.
Variation of the $Fe^{(III)}$ TMPP membrane resistance (R_m) plots versus $p[X]$.

Figure 8.
Variation of the $Fe^{(III)}$ TMPP charge transfer resistance (R_{ct}) plots versus $p[X]$.

The R_{ct} slope values of the Au transducer coated by $Fe^{(III)}$ TMPP membrane for the impedimetric detection of BPA, 2,2'-biphenol and catechol are illustrated in **Table 1**. As can be seen, the slope associated with the catechol molecule has a lower

Sensitive membrane	Analytes	R _{ct} slope (kΩ/decade)
Fe ^(III) TMPP	bisphenol A	2.104
	2,2'-biphenol	1.770
	catechol	0.983

Table 1.
Comparison of the R_{ct} slope values of Au/Fe^(III)TMPP electrode for different phenolic analytes.

Figure 9.
Chemical structure of BPA, 2,2'-biphenol and catechol showing the presence of two aromatic rings in bisphenol A and 2,2'-biphenol and the presence of one aromatic ring in catechol.

value, whereas the slope associated with BPA and 2,2'-biphenol molecules has a higher value. These results show a better sensitivity of Fe^(III)TMPP towards BPA molecules. This can be explained by the higher number of aromatic groups in the structures of BPA and 2,2'-biphenol than in the structure of catechol (**Figure 9**). According to these results, we have chosen BPA as the target molecule for Fe^(III)TMPP membrane throughout our next measurements.

4. BPA sensor based on carbon nanotubes/Fe^(III)TMPP nanocomposite

In order to enhance the sensitivity of the Fe^(III)TMPP towards the detection of BPA, carbon nanotubes (CNTs) has been used to dope iron (III) porphyrin as it has attracted considerable interest due to its excellent electrochemical properties and its high ability to amplify the detection signal [38, 39]. Hence, Fe^(III)TMPP was doped

Figure 10.
Nyquist diagrams of (A) Au/2%CNTs/Fe^(III)TMPP electrode and (B) Au/4%CNTs/Fe^(III)TMPP electrode for different BPA concentrations.

Figure 11.
Schematic presentation of the non-interaction of most aromatic rings of $\text{Fe}^{(\text{III})}\text{TMPP}$ with CNT because of their unsuitable structures.

by 2% CNTs and 4% CNTs, then the obtained 2% CNTs/ $\text{Fe}^{(\text{III})}\text{TMPP}$ and 4%CNTs/ $\text{Fe}^{(\text{III})}\text{TMPP}$ nanocomposites have been used for the detection of different concentrations of BPA (**Figure 10**). As can be seen, the Nyquist plots of 2%CNTs/ $\text{Fe}^{(\text{III})}\text{TMPP}$ and 4%CNTs/ $\text{Fe}^{(\text{III})}\text{TMPP}$ modified Au electrodes show a very small variation with increasing BPA concentrations. This result shows that the doping of porphyrin by CNTs did not improve its sensitivity towards the detection of BPA molecules. This can be explained by the planar structure of $\text{Fe}^{(\text{III})}\text{TMPP}$ making difficult the π - π interaction with the rolled up tubular structure of CNT (**Figure 11**). These results led us to think about improving the sensitivity of the Au/ $\text{Fe}^{(\text{III})}\text{TMPP}$ sensor using another carbon material having a 2D planar structure which can make easier the π - π interaction with $\text{Fe}^{(\text{III})}\text{TMPP}$ and preserves its structure. Because of its fascinating electronic properties and extremely high specific surface area, this chosen carbon material is known as reduced graphene oxide (RGO), a graphene derivate that has attracted a lot of attention in improving the sensing ability of BPA sensors [40].

5. BPA sensor based on nanocarbon transducer functionalized by $\text{Fe}^{(\text{III})}\text{TMPP}$

After proving the good affinity of $\text{Fe}^{(\text{III})}\text{TMPP}$ towards BPA molecules, we aim to improve the sensitivity of Au/ $\text{Fe}^{(\text{III})}\text{TMPP}$ sensor by involving the use of nano-sized electrodes based on nanocarbon transducers. Hence, owing to its strong electrocatalytic activity and minimal surface fouling, RGO has been chosen as a nanocarbon material to functionalize it on Au electrode to form a new Au/RGO nanocarbon transducer with enhanced charge transfer ability than the Au transducer. Then, the Au/RGO nanocarbon transducer has been prepared and functionalized with $\text{Fe}^{(\text{III})}\text{TMPP}$ membrane to form Au/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ platform.

With the objective of highlighting the interaction between the $\text{Fe}^{(\text{III})}\text{TMPP}$ and the Au/RGO nanocarbon transducer, UV/vis has been used. Hence, the prepared ITO/RGO, ITO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ and ITO/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ electrodes were characterized by UV-vis (**Figure 12**). As shown in **Figure 12**, the UV/vis absorption spectrum of ITO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ exhibits a strong peak at 438 nm and a weak peak at 527 nm ascribed to the Soret band and the Q-band of porphyrin respectively. After we have deposited the $\text{Fe}^{(\text{III})}\text{TMPP}$ on ITO/RGO, we have observed a decrease in the Soret and Q band intensities with a red shift from 438 nm to 431 nm for the Soret band and the Q-band shift from 527 nm to 536 nm. These shifts prove the strong π - π interactions between the aromatic rings of RGO and the $\text{Fe}^{(\text{III})}\text{TMPP}$ macrocycles [41, 42]. These results confirm the formation of the graphene-porphyrin complex, being in agreement with the proposed hypothesis of the easier interaction of the flattened structure of porphyrin with the 2D surface of graphene (**Figure 13**).

Bare Au, Au/ $\text{Fe}^{(\text{III})}\text{TMPP}$, Au/RGO and Au/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ electrodes have been characterized by EIS in PBS (0.1 M, pH = 7) with an optimized potential of -0.9 V (**Figure 14**).

As shown in **Figure 14**, the total impedance plot of Au/RGO shows a semi circle with a diameter smaller than obtained with bare Au. Consequently, the R_{ct} value of Au/RGO decreased compared to that of bare Au. This result proves that the fabricated Au/RGO nanocarbon transducer has improved charge transfer ability than the usual transducer (Bare Au) thanks to the electron catalyst role of RGO. As illustrated in **Figure 14**, the impedance plot of Au/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ structure presents a very smaller semi circle diameter compared to Au/ $\text{Fe}^{(\text{III})}\text{TMPP}$ electrode which is explained by smaller R_{ct} value for Au/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$, thus better charge transfer ability at the interface electrode/electrolyte. This result demonstrates that the Au/RGO nanocarbon transducer ensured the good attachment of the porphyrin on its surface via π - π interaction as we have proved by UV-visible which leads to enhanced kinetic charge transfer of the Au/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ structure.

Figure 12. UV/vis spectra of ITO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ and ITO/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ structures.

Figure 13.
Schematic presentation of the π - π interaction between aromatic rings of $\text{Fe}^{(\text{III})}\text{TMPP}$ and RGO thanks to their planar structures.

Figure 14.
Nyquist plot of Bare Au, $\text{Au}/\text{Fe}^{(\text{III})}\text{TMPP}$, Au/RGO and $\text{Au}/\text{RGO}/\text{Fe}^{(\text{III})}\text{TMPP}$ electrodes in PBS (0.1 M, pH = 7).

The Nyquist diagram of $\text{Au}/\text{RGO}/\text{Fe}^{(\text{III})}\text{TMPP}$ electrode, as shown in **Figure 15**, reveals the presence of a small semicircle at high frequency, corresponding to a small phase pic maxima in the phase diagram, and a large second semicircle at low

Figure 15.
Nyquist and Bode plots of the Au/RGO/Fe^(III)TMPP electrode with the fit result.

frequency, corresponding to an intense phase pic maxima in the phase diagram. Hence, the proposed equivalent electrical circuit should be composed by more than one dipole [28]. The best fit was done using an equivalent electrical circuit formed by a parallel association of two dipoles placed in series with the electrolyte resistance (R_s) (**Figure 16**). The first dipole, which is attributed to the high frequency loop and the electrochemical phenomena occurring at the electrolyte/membrane interface, was formed by a membrane resistance (R_m) and a membrane capacitance (C_m). The second dipole, is attributed to the second loop at low frequencies and describes the electrochemical phenomena taking place at the membrane/electrode interface, was composed of charge transfer resistance (R_{ct}) and constant phase element (CPE).

The sensing properties of Au/RGO/Fe^(III)TMPP electrode towards BPA concentrations in PBS electrolyte have been studied and presented in **Figure 17**. The semicircle diameter related to the charge transfer resistance (R_{ct}) from the RGO/Fe^(III)TMPP to the electrode is observed to increase upon the addition of BPA concentration. This considerable dependance affirms the high affinity of Au/RGO/Fe^(III)TMPP sensor towards BPA molecules.

Figure 16.
Equivalent circuit used to fit the impedance spectra of Au/RGO/Fe^(III)TMPP electrode.

Figure 17.
EIS responses of the Au/RGO/Fe^(III)TMPP electrode in the absence and the presence of different BPA concentrations.

The electrical parameters values of Au/RGO/Fe^(III)TMPP electrode after BPA attachment were obtained from the equivalent circuit model presented in **Figure 16**. Then a comparative study of R_m and R_{ct} variations versus $p[BPA]$ for Au/Fe^(III)TMPP and Au/RGO/Fe^(III)TMPP electrodes has been studied (**Figure 18**).

As can be observed in **Figure 18**, R_m and R_{ct} variations increase with the successive addition of BPA concentration for the Au/Fe^(III)TMPP and Au/RGO/Fe^(III)TMPP electrodes. This result confirms the adsorption mechanism of BPA on the surface of the two modified electrodes, resulting in an increase of their

Figure 18.
Variation of the relative changes of (A) the membrane resistance and (B) the charge transfer resistance of Au/Fe^(III)TMPP and Au/RGO/Fe^(III)TMPP electrodes versus BPA concentration cologarithm ($p[BPA]$).
 $\Delta R_{ct} = R_{ct} - R_{cto}$ where R_{ct} is the charge transfer resistance of the sensing membrane for each BPA concentration and R_{cto} is the charge transfer resistance without any addition of concentration.

Electrodes	Slope of R_m variation	Slope of R_{ct} variation
Au/Fe ^(III) TMPP	0.1147	0.2285
Au/RGO/Fe ^(III) TMPP	0.2598	0.4218

Table 2.
Comparison of the R_m and R_{ct} variations slopes values of Au/Fe^(III)TMPP and Au/RGO/Fe^(III)TMPP electrodes for BPA detection.

thickness membranes correlated with a decrease of the electron transfer ability at the membrane/electrode interface. The slope of R_m and R_{ct} variations curves versus p[BPA] for Au/Fe^(III)TMPP and Au/RGO/Fe^(III)TMPP electrodes are summarized in **Table 2**. This table shows that the slopes of R_m and R_{ct} variations curves obtained with Au/RGO/Fe^(III)TMPP electrode are 2 times higher than those obtained with Au/Fe^(III)TMPP electrode. This result proves the doubled sensitivity with the Au/RGO/Fe^(III)TMPP electrode towards BPA. This improved sensitivity comes from the catalyst role of RGO [43] which has created a nanocarbon transducer with enhanced electrical property and signal transfer. Based on the calibration curve (**Figure 18B**), the sensitivity (slope of the calibration curve) of our proposed sensor Au/RGO/Fe^(III)TMPP was found to be 0.4218 per decade with an intercept of 5.6509. The correlation regression coefficient was obtained at 0.9987 in the concentration range from 10^{-12} M to 10^{-8} M. The detection limit of the sensor was estimated to be 2.1×10^{-13} M (signal-to-noise ratio of 3 independent measurements).

6. Comparative study

Because of the biologically harmful and toxicologically relevant of BPA even at low doses, researchers are competing to develop a new electrochemical sensor to track low BPA levels. **Table 3** illustrates a comparison of the analytical performances between our BPA sensor based on RGO nanocarbon transducer (Au/RGO/Fe^(III)TMPP) and other recently reported BPA sensors. Alam et al. reported graphene oxide and β -cyclodextrin functionalized multiwalled carbon nanotubes (GO-MWCNT- β CD) for the detection of BPA at nanomolar level (6 nM) with good reproducibility (n = 3) and a two-step linear response from 0.05 to 5 μ M and 5–30 μ M [44]. The GO-MWCNT- β CD modified screen-printed electrode (SPE) showed the highest oxidation peak current of 49.4 μ A at Epa of 595 mV for BPA, which is at least 1.6 times higher than other modified SPEs. This was explained by the synergistic effect between GO, MWCNT and β CD leading to a fast electron transfer kinetics, consequently an amplified signal detection of BPA. Wan et al. reported an eco-friendly electrochemical sensor based on Multi-Walled Carbon Nanotubes (MWCNT)/Polythiophene(PTh)/Pt nanocomposites-modified glassy carbon electrode for determination of BPA molecules in aqueous media [45]. The working electrode captures BPA electrochemically and consequently gets adsorbed on the MWCNT-PTh-Pt electrode surface electrode followed by electrochemical oxidation by differential pulse voltammetry (DPV) with the increased oxidation current at 0.5 V. This affinity was explained by the Pt nanocluster that acted as a suitable catalyst of MWCNT-PTh nanocomposite and enhanced the electrochemical detection signal of BPA. Moreover, this sensor platform revealed linear response for BPA detection from 0.005 to 0.4 μ M in phosphate buffer saline (PBS) solution and the detection limit was found to be 0.003 μ M (S/N = 3). Ponnaiah et al. designed a GCE modified with a new nanocomposite composed of ruthenium nanoparticles, polyaniline and graphitic carbon nitride (Ru⁰/PANI/g-C₃N₄) as an electrochemical

Sensor material	Detection method	LOD (μM)	Linear range (μM)	Preparation method of the sensor	Reference
GO-MWCNT- βCD /SPE	LSV	6	0.05–5/5–30	Covalent modification of MWCNTs with βCD / drop casting of GO-MWCNT- βCD suspension on SPE	[44]
MWCNT/PTh/Pt/GCE	DPV	3.0×10^{-3}	0.005–0.4	Electrodeposition of MWCNT-PTh-Pt on GCE	[45]
$\text{Ru}^0/\text{PANI@g-C}_3\text{N}_4$	DPV	0.18×10^{-3}	0.01–1.1	Long time ultrasonication of the $\text{Ru}^0/\text{PANI/g-C}_3\text{N}_4$ nanocomposite / drop casting of $\text{Ru}^0/\text{PANI/g-C}_3\text{N}_4$ suspension on GCE	[46]
ND-GCE	SWV	13×10^{-3}	0.1–80	Ultrasonication of ND in water followed by drop casting on GCE	[47]
AgNPs-EG	SWV	0.23	5.0–100	Long term preparation of AgNPs-EG electrode	[48]
Au/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$	EIS	2.1×10^{-7}	10^{-6} – 10^{-2}	Simple and fast ultrasonication of RGO and $\text{Fe}^{(\text{III})}\text{TMPP}$ /drop casting deposition of RGO and $\text{Fe}^{(\text{III})}\text{TMPP}$ on Au electrode respectively	This work

Table 3.
Comparison of the detection method, detection limit, linear range and preparation method of the sensor of recently reported sensors and the present study for the determination of BPA.

sensor for the detection of BPA [46]. The sensor system exhibits picomolar-level detection limits, good sensitivity and stability with a detection range from 0.01 to 1.1 μM . This result was explained by the synergistic effect of the nanocomposite: the high activity of ruthenium nanoparticles, the porous structure of the conducting PANI and the catalyst role of g- C_3N_4 that created an amplified detection system. Jiang et al. reported the development of electrochemical sensors based on carbon nanomaterials, i.e. nanodiamond (ND/GCE) and nanocarbon (NC/GCE) [47]. These carbon materials have achieved a good sensitivity towards BPA monitored by Square Wave Voltammetry (SWV) thanks to their low fouling properties and porous structures. The limit of detection of the proposed sensor was at the nanomolar level with an acceptable liner range from 0.1 to 80 μM . Tsekeli et al. reported the synthesis of silver nanoparticle-exfoliated graphite nanocomposite (AgNPs-EG) for the application of BPA sensor [48]. The AgNPs-EG nanocomposite-based electrode has demonstrated antifouling property and acceptable affinity towards BPA with LOD of 0.23 μM and a linear range from 5.0 to 100 μM .

Compared with all these recently reported BPA sensors (**Table 3**), our work based on Au/RGO/ $\text{Fe}^{(\text{III})}\text{TMPP}$ sensor presents the best sensing platform because of its lower limit of detection in the picomolar level (2.1×10^{-7} μM) and wider linear range spreading from 10^{-6} to 10^{-2} μM . Hence, the sensor based on nanocarbon transducer functionalized by $\text{Fe}^{(\text{III})}\text{TMPP}$ presented in this work is capable of measuring BPA at concentrations lower than the daily dose limits set by recent medical advice. In addition to a lower detection limit and wide detection range, our fabrication method is based only on drop-casting and drying, which is more facile and less time consuming than other methods. Furthermore, the modification of our sensor is based on non-covalent bonding which preserves the sp^2 structures of each membrane, leading to a good stability of the BPA response signal. Another advantage of our proposed sensor was that, in our work, electrochemical impedance

spectroscopy was used to follow the detection signal of BPA, while it was rarely used compared to DPV and SWV methods to monitor the attachment of BPA on the sensor surface. The advantage of the EIS method compared to the most frequently used SWV and DPV methods is that it does not damage the electrode surface and also enables low detection limits [49]. We envisage that such sensors are promising tools to face the challenges of the detection of BPA at trace level in aqueous media, as an alternative to the conventional test or central lab equipment.

The better sensing performance of our sensor based on Au/RGO/Fe^(III)TMPP could be attributed to different aspects such as the architecture of the modified electrode that is based on Au/RGO nanocarbon transducer for immobilized Fe^(III)TMPP to retain its stability and activity which can facilitate the reaction towards BPA. Moreover, the high electric conductivity of RGO nanocarbon material can create a novel nanocarbon transducer with higher kinetic charge transfer compared to usual used transducers which facilitates the mediation of electrocommunication between the BPA and the electrode.

7. Conclusions

In this chapter, a label-free impedimetric sensor using Au/RGO nanocarbon transducer functionalized by Fe^(III)TMPP has been successfully designed for the detection of trace BPA. The Au/RGO/Fe^(III)TMPP electrode was fabricated by loading RGO and Fe^(III)TMPP membrane on Au transducer, respectively. The Au/RGO/Fe^(III)TMPP sensor has demonstrated an amplified response towards BPA compared to that of Au/Fe^(III)TMPP electrode. This enhancement was attributed to the Au/RGO nanocarbon transducer which acted as a charge transfer catalyst and good platform for the attachment of Fe^(III)TMPP via π - π stacking. The suggested Au/RGO/Fe^(III)TMPP has offered a few advantages compared to the previously reported strategy for the determination of BPA, including excellent low LOD (2.1×10^{-13} M) and wide linear dynamic range with a simple and efficient fabrication method. The findings from this study will be valuable for constructing highly sensitive sensors based on modified Au/RGO nanocarbon transducer to detect various substances with low concentration and trace amount.

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