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# Development of highly sensitive and selective bisphenol A sensor based on a cobalt phthalocyanine-modified carbon paste electrode: application in dairy analysis

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The development of an accurate, sensitive and selective sensor for the detection of bisphenol A (BPA) based on the incorporation of a new phthalocyanine derivative, cobalt phthalocyanine, C,C,C,C-tetracarboxylic acid-polyacrylamide (CoPc-PAA) into a carbon-paste matrix is presented using voltammetry and constant potential techniques. The influence of measuring parameters such as pH and scan rate on the analytical performance of the sensor was evaluated. Several kinetic parameters such as electron transfer number ( $n$ ), charge transfer coefficient ( $\alpha$ ), electrode surface area ( $A$ ) and diffusion coefficient ( $D$ ) were also calculated. Under optimum conditions, particularly at pH 7.2, the BPA sensor resulted in a wide linear range from  $25 \times 10^{-11}$  M to  $2.5 \times 10^{-7}$  M and a limit of detection as low as 63.5 pM. Based on these findings, it can be concluded that our sensor can be substantially utilized for detecting BPA in spiked milk samples.

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## 1. Introduction

2,2-Bis-(4-hydroxyphenyl)propane (bisphenol A, BPA) is widely used in industry as a raw material in the synthesis of polycarbonate (PC), polyacrylate, and polysulfone and as a component of food packaging, nursing bottles, food can linings and beverage containers. Research has shown that BPA can leach from beverages or food containers, leading to the human exposure of trace amounts of BPA. BPA can transfer from polycarbonate to liquid food through two different processes: diffusion of residual BPA present in the bottle after the manufacturing process and hydrolysis of the ester linkage that binds it to the polycarbonate or resin, depending on temperature, acidity and alkalinity.<sup>1</sup>

BPA is a potential endocrine-disrupting chemical and according to reports it may interfere with numerous biological functions.<sup>2</sup> BPA contains a phenolic group whose molecular structure is similar to that of endocrine hormones (such as estradiol and diethylstilbestrol) and has an affinity for estrogen binding agents. Therefore, it is harmful to human health even at low concentrations;<sup>3</sup> for example, 1 nM BPA may interfere with the function of adiponectin in human adipose tissue,<sup>4</sup> leading to

diabetes and cardiovascular disease and female habitual abortion,<sup>5,6</sup> In addition, it is thought that bisphenol A can cause a decline in human sperm quality, and various kinds of cancers.<sup>7-9</sup> The Food and Drug Administration (FDA) set a dose limit of BPA at 40 mg kg<sup>-1</sup> body weight (bw)/day,<sup>10</sup> adjusted to 4 mg/kg bw/day by the European Food Safety Authority.<sup>11</sup> However, a recent discovery by Consortium Linking Academic and Regulatory Insights on BPA Toxicity (CLARITY BPA) showed that the incidence of breast cancer in rodents increased significantly when BPA doses were administered at 2.5 mg kg<sup>-1</sup> bw/day. Studies have shown that even low-dose bisphenol A has biohazard and toxicological significance. Therefore, the effective measurement of low levels of BPA is essential in reducing BPA exposure.

When designing a rapid quantitative approach for BPA, a sensitive and simple technique is of particular importance. Concerns about the possible serious effects of BPA have prompted the use of liquid chromatography (HPLC, UPLC),<sup>12</sup> gas chromatography-mass spectrometry (GC-MS),<sup>13</sup> fluorescence,<sup>14</sup> and enzyme linked immunosorbent assays.<sup>15</sup> While these techniques provide highly sensitive detection and accurate identification, they however have several limitations, such as complex pretreatment stages, being labor-intensive and the requirement for expensive equipment. An alternative to these costly methods is the use of electrochemical sensors whose sensitivity, portability, rapid time to result and low cost have been used for environmental monitoring<sup>16,17</sup> and food processing,<sup>18</sup> in addition to medical diagnosis.<sup>19</sup>

Herein, for the determination of BPA, different types of electrodes including imprinted polymers,<sup>20</sup> sonogel-carbon<sup>21</sup>

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screen-printed electrode (SPE),<sup>22</sup> micropaper-based analytical device ( $\mu$ PAD)<sup>23</sup> glassy carbon electrode,<sup>24</sup> and carbon paste electrode (CPE)<sup>25</sup> have been used. Among them, CPE is most often used due to its low cost, ease of preparation, quick surface renewal, great versatility, wide potential window, low ohmic resistance and compatibility with various types of modifiers.

BPA has previously been detected using an oxidation reaction with an electrochemically active electrode material such as carbon or graphite.<sup>26</sup> The oxidation of BPA may result in by products that contribute to low sensitivity and selectivity.<sup>27</sup> These effects may be overcome by electrode modification. Many materials containing metals or metal alloys, various nanotubes and nanoparticles, graphene and fullerenes, phthalocyanine and their derivatives, and some organic dyes are widely used for constructing electrochemical sensors.<sup>28–30</sup>

Metal phthalocyanines (MPcs) are an abundant class of small molecules composed of a highly conjugated cyclic structure with a central chelated metal ion. The use of MPcs relies upon their redox properties, high chemical and thermal stabilities, design flexibility, and interesting electrochemical properties.<sup>31</sup> Due to the macrocyclic nature of the extended  $\pi$  system, phthalocyanine can undergo rapid redox processes.<sup>32</sup> The central metal ion may be inert to redox processes (*e.g.* Ni(II)) or may be a transition metal such as Fe(II) that undergoes a redox process at potentials comparable to the phthalocyanine ring processes.

Due to their interesting redox properties, transition metal phthalocyanine complexes have been used as sensing materials for the detection of some biologically and environmentally important compounds, such as O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, nitrites, thiols, thiocyanate, dopamine and epinephrine.<sup>33–35</sup> The catalytic behavior of cobalt phthalocyanine (CoPc) is related to Co(II)/Co(III) or Co(II)/Co(I) redox processes in CoPc complexes.<sup>36</sup> However, one of the main problems of physically adsorbed CoPc is that the electroactive material can be unstable and is gradually removed, resulting in a decrease in electrochemical activity, which, together with low conductivity, makes it necessary to have a suitable microenvironment for encapsulation that improves the rate of electron transfer.

Herein, the aim of this study is to develop a simple and highly sensitive electrochemical method for the determination of bisphenol A based on the incorporation of a novel cobalt phthalocyanine derivative and C,C,C,C-tetracarboxylic acid-polyacrylamide (CoPc-PAA) into a graphite-modified carbon paste electrode (CPE). The newly proposed method possesses some advantages including high sensitivity, extreme simplicity, rapid response and low cost. We have also evaluated the analytical performances of the developed sensor for the quantification of BPA in spiked milk samples.

## 2. Materials and methods

### 2.1. Chemicals and electrochemical characterisation apparatus

The cobalt phthalocyanine C,C,C,C-tetracarboxylic acid-polyacrylamide (CoPc-PAA) molecule used in this study was synthesised and purified according to ref. 37 and its structural, optical and electrical properties have been characterised in our

previous work<sup>38</sup> *via* RAMAN and UV-Vis spectroscopy studies, showing (i) the metal phthalocyanines characteristic vibronic bands and (ii) B and Q characteristics bands located at 270 nm and 657 nm, respectively, in addition to an energy band gap of about 3.34 eV in the presence of trapping levels at 1.78 eV and 1.90 eV similar to those found in the literature for cobalt phthalocyanine derivatives.<sup>38</sup>

Bisphenol A (99.0%), Nujol oil, graphite powder (fine powder pure pH 5–6 (50 g L<sup>-1</sup>, H<sub>2</sub>O, 20 °C)) and solvents were purchased from Sigma-Aldrich. All chemicals were of analytical grade and used without any further purification. Phosphate buffer saline (PBS) was used as the supporting electrolyte and prepared using 0.1 M KCl, 0.1 M of KH<sub>2</sub>PO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub>. Working solutions were freshly prepared before use. Cyclic voltammetry (CV), chronocoulometry (CC) measurements were performed on a CHI 920 electrochemical workstation. All electrochemical experiments were carried out with a three-electrode system: unmodified CPE or CPE/CoPc-PAA was used as the working electrode, a platinum wire electrode was used as the counter electrode, and an Ag/AgCl (3 M KCl) electrode was used as the reference electrode.

### 2.2. Electrode preparation

The carbon paste electrodes were prepared according to reported procedures<sup>39</sup> using a 70/30 (w/w) mixture; 0.6 g of Nujol oil (binder) and 2 g of graphite powder.

The as-prepared paste was packed into a 3 mm glass tube, with contact provided by a copper wire. Before use, the surface of CPE was renewed by polishing on a smooth paper. Modified CPEs were prepared in the same manner, except that 1% w/w of CoPc-PAA was added to the graphite powder in the initial step.

## 3. Results and discussion

### 3.1. Selection of a suitable electrolyte for bisphenol A quantitation

Due to the relatively low solubility of BPA in water, three organic solvents (methanol, ethanol and acetonitrile), were selected as

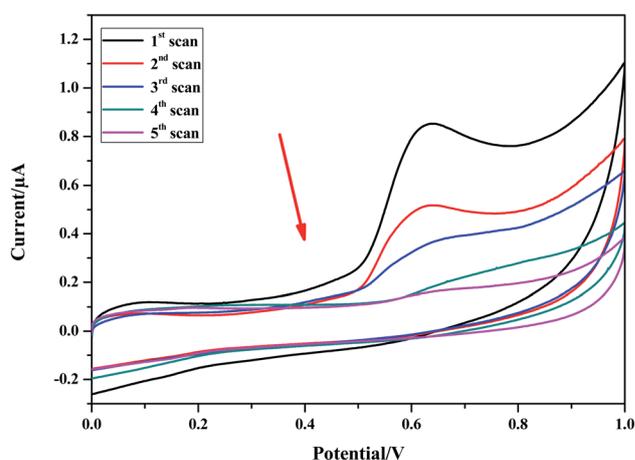


Fig. 1 Cyclic voltammetry of 0.1 mM BPA in PBS and acetonitrile (20%) at the carbon paste electrode (pH 7.0, scan rate 100 mV s<sup>-1</sup>).

solvents. The highest current response and the lowest oxidation potential were observed in acetonitrile, and it was chosen as the co-solvent to dissolve BPA together with electrolyte. In addition, the influence of % acetonitrile in the working solution on the voltammetric response of BPA was investigated. Various amounts of acetonitrile were added to the volumetric flask and diluted with PBS to adjust the pH to 7.0 (BPA was 2.5 mM). The highest response was obtained in a solution containing 20% (v/v) acetonitrile.

### 3.2. Voltammetric response of bisphenol A

Fig. 1 shows CV traces of BPA (0.1 mM) oxidation at the carbon paste electrode. In the forward sweep, the oxidation peak appears at 0.62 V (vs. Ag/AgCl) with no reverse wave, indicating the irreversible electrochemical reaction of BPA on the

electrode. With successive CV scans, the anodic response decreased significantly as BPA underwent oxidation, and follow on chemical products/oligomers prevent further interaction of the BPA monomer with the electrode.

Cyclic voltammograms of 2.5  $\mu$ M BPA (Fig. 2) were recorded using both unmodified and modified CPE in 0.1 M phosphate/acetonitrile (20%) buffer (pH 7.0) over the potential range of 0–1 V vs. Ag/AgCl. The direct oxidation of the BPA compounds at the unmodified CPE displayed a very weak anodic peak at 0.68 V vs. Ag/AgCl, which is in line with previous reports.<sup>40–42</sup> For the CoPc-PAA-modified electrode, the anodic peak current, was highly enhanced relative to the unmodified electrode ( $E_p = 0.64$  V vs. Ag/AgCl). Upon cycling, the current decreased because of electrode fouling resulting in a passivating phenolic film, which was initiated upon oxidation.<sup>43–47</sup>

### 3.3. pH effects

The BPA voltammetric response at a modified CPE over the pH range of 4.2–7.8 is shown in Fig. 3A. Considering the sensitivity of the determination of BPA, a pH value of 7.2 was selected for subsequent analytical experiments.

The cathodic shift in the oxidation potential  $E_p(a)$  with the increase in pH indicated that protons are directly involved in the process, as shown in Fig. 3B; the pH values and  $E_{pa}$  are linearly associated according to the following equation:  $E_{pa} = -0.05046 \text{ pH} + 1.10748$ ; ( $R^2 = 0.9184$ ). A slope of  $50 \text{ mV pH}^{-1}$ , being close to the theoretical value of  $0.0576 \text{ V pH}^{-1}$ , clearly indicates equal loss of electrons and protons during the BPA electrochemical oxidation reaction.<sup>48</sup>

### 3.4. Effects of scan rate

Useful information involving the electrochemical mechanism can usually be acquired from the relationship between the peak current and the scan rate. Fig. 4A shows the cyclic

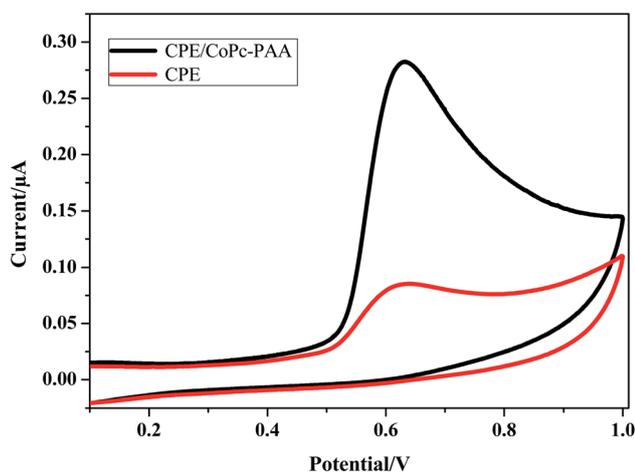


Fig. 2 Cyclic voltammograms of 2.5 mM BPA in 0.1 M PBS/acetonitrile 80%:20% (v/v) at bare CPE (black) and CPE/CoPc-PAA (red) (pH 7.0; scan rate  $100 \text{ mVs}^{-1}$ ).

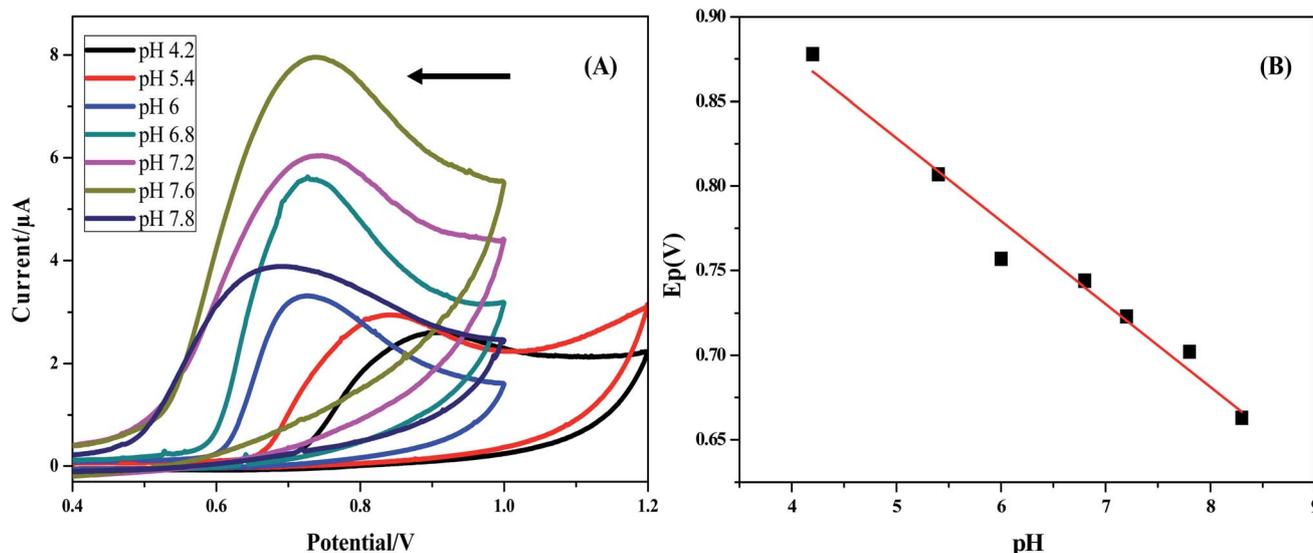


Fig. 3 (A) Cyclic voltammograms showing response to 2.5 mM BPA at CPE/CoPc-PAA in phosphate buffer over the pH range of 4.2–7.8. (B)  $E_{pa}$  as a function of pH.

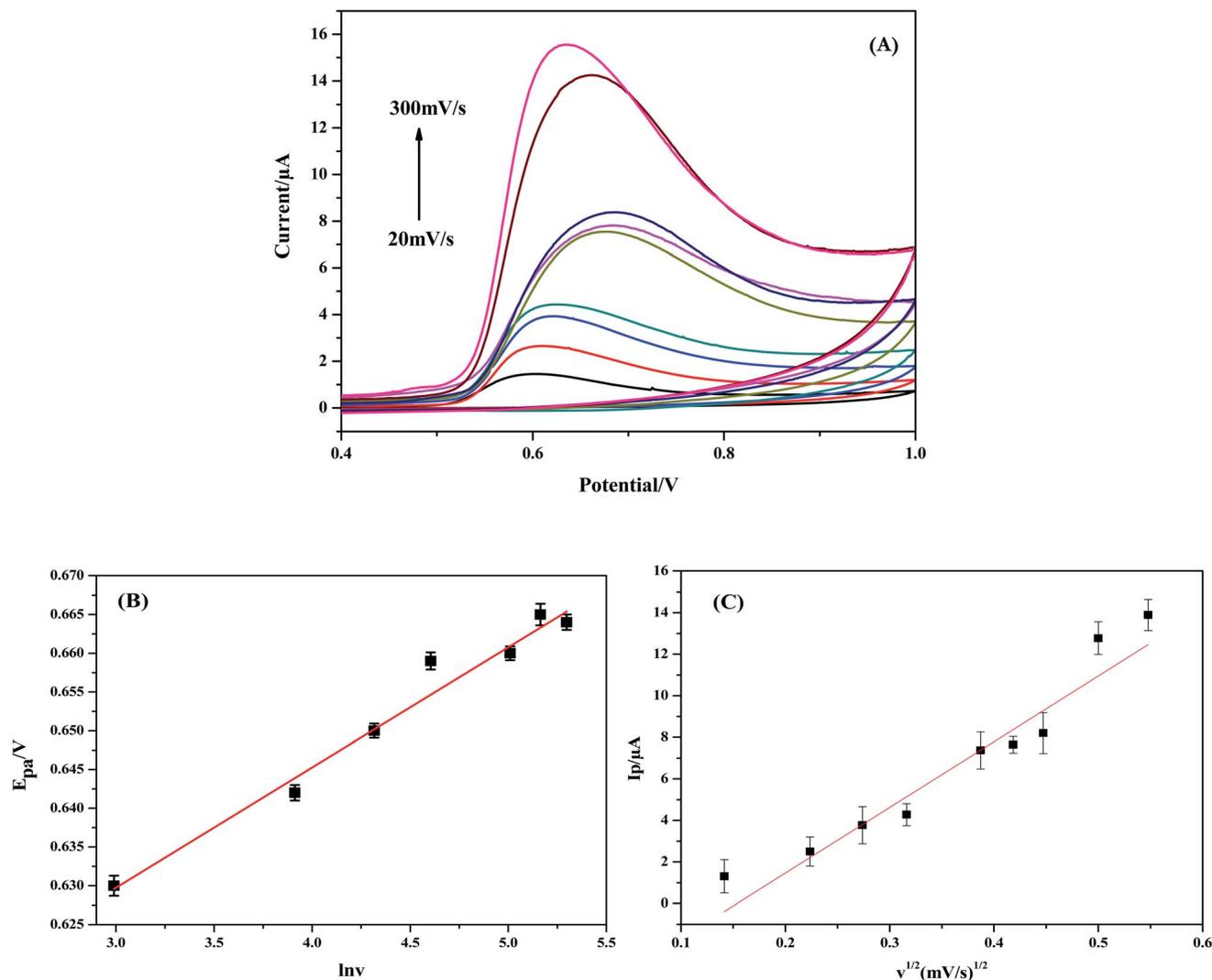


Fig. 4 (A) Cyclic voltammograms of 2.5 mM BPA at CPE/CoPc-PAA over the range of 20–300  $mV s^{-1}$ . (B) The relationship between  $E_{pa}$  and  $\ln \nu$ . (C) The relationship between  $I_{pa}$  and  $\nu^{1/2}$ .

voltammograms for 2.5 mM BPA at CPE/CoPc-PAA over the range of 20–300  $mV s^{-1}$  with a linear relationship evident between current and scan rate – the linear regression equation can be estimated as:  $I_{pa}(\mu A) = 34.9\nu - 5.45$ . The value of the linear correlation coefficient was 0.934, which suggested that the oxidation process of BPA on the electrode was controlled by surface adsorption due to follow on chemical processes. Peak potential  $E_p(a)$  plotted against  $\ln \nu$  (Fig. 4 B) was expressed as follows:  $E_p(a) = 0.0156 \ln \nu + 0.582$ ; ( $R = 0.967$ ).

The relation between the square root of the scan rate and the peak current (Fig. 4C) indicated a linear correlation ( $n = 3$ ) over the range of 20–300  $mV s^{-1}$  with equation  $I_p (\mu A) = 3.16 \times 10^{-5}\nu^{1/2}$  to  $4.85 \times 10^{-6}$  ( $R^2 = 0.935$ ) resulting in a mixed diffusion/adsorption process for the oxidation of BPA.

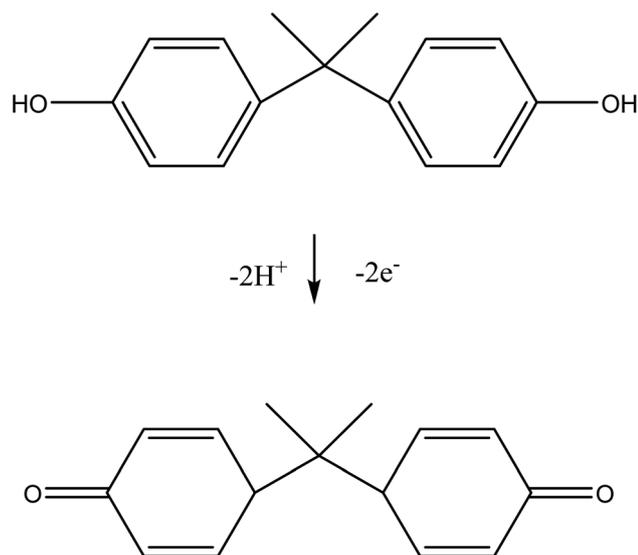
For a totally irreversible electrode process, the relationship between  $E_{pa}$  and  $\ln \nu$  is defined by Laviron<sup>49</sup> as follows:

$$E_{pa} = E_0 + \frac{RT}{\alpha nF} \ln \frac{RTk_0}{\alpha nF} + \frac{RT}{\alpha nF} \ln \nu \quad (1)$$

where  $\alpha$  is the transfer coefficient;  $k_s$  is the standard heterogeneous rate constant of the reaction,  $n$  is the number of transferred electrons,  $\nu$  is the scan rate,  $E_0$  is the formal redox potential,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $F$  is the Faraday constant ( $T = 298$  K,  $R = 8.314$  J  $K^{-1}$   $mol^{-1}$ , and  $F = 96485$  C  $mol^{-1}$ ). The value of  $\alpha n$  was calculated from the slope and was estimated as 0.93, indicating a 2-electron oxidation process, which agrees with other published reports.<sup>50–52</sup> The BPA electro-oxidation process can be described as follows (Scheme 1).

### 3.5. Chronocoulometric studies

The effective surface areas of CPE and CPE/CoPc-PAA was investigated *via* chronocoulometry (using 0.1 mM  $K_3[Fe(CN)_6]$  as a redox probe) and was calculated from the slope of the plot of  $Q$  vs.  $t^{1/2}$  (Fig. 5) according to the integrated Cottrell eqn (2):<sup>53,54</sup>



Scheme 1 Electrooxidation process of BPA at CPE/CoPc-PAA.

$$Q = 2nFACD^{1/2}t^{1/2}\pi^{-1/2} \quad (2)$$

where  $A$  is the effective surface area of the working electrode,  $C$  is the concentration of the substrate,  $n$  is the number of electrons and  $D$  is the diffusion coefficient,  $D$  of  $K_3[Fe(CN)_6]$  is  $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,<sup>55</sup> and  $F$  is the Faraday's constant ( $F = 96485 \text{ C mol}^{-1}$ ). Based on the slope of the linear relationship between  $Q$  and  $t^{1/2}$ , the effective surface area  $A$  was calculated to be  $0.014 \text{ cm}^2$  and  $0.0307 \text{ cm}^2$  for CPE and CPE/Co-Pc, respectively.

The diffusion coefficient  $D$  and  $Q_{\text{ads}}$  for BPA at the modified electrode were also determined based on the expression below (3)

$$Q(t) = 2nFAcD^{1/2}t^{1/2}\pi^{-1/2} + Q_{\text{dl}} + Q_{\text{ads}} \quad (3)$$

where  $Q_{\text{dl}}$  is a double layer charge, which could be eliminated by background subtraction and  $Q_{\text{ads}}$  represents the adsorbed contribution. From the slope and intercept of the plot of  $Q$  vs.  $t$  (Fig. 6A), the values of  $D$  and  $Q_{\text{ads}}$  can be obtained. After background subtraction, the plot of  $Q$  against  $t^{1/2}$  (Fig. 6B) showed a linear relationship with slope of  $1.83 \times 10^{-5}$  and  $Q_{\text{ads}}$  of  $1.45 \times 10^{-6} \text{ C}$ . As  $n = 2$ ,  $A = 0.0307 \text{ cm}^2$  and  $C = 2.5 \text{ mM}$ ,  $D$  was calculated as  $1.689 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , which is in the same range for the value of  $D$  in the work of H. Yin *et al.*<sup>56</sup>

According to the eqn (4):

$$Q_{\text{ads}} = nFA\Gamma_s \quad (4)$$

$\Gamma_s$  the surface coverage was calculated to be  $1.04 \times 10^{-11} \text{ mol cm}^{-2}$ .

### 3.6. Reproducibility and interferences

The reproducibility of the sensor was examined by testing each concentration three times. The resulting relative standard deviation (RSD) was 6.3% for three determinations by an independently prepared sensor. The experimental results have indicated good reproducibility of the fabrication protocol.

The selectivity of the electrochemical sensor towards BPA was investigated in the presence of some possible interfering substances at concentrations 100-fold higher than that of BPA. Some common phenolic complexes and inorganic ions were tested to check their levels of interference with BPA determination. The tolerance limit was defined as the maximum concentration of the interfering substance that causes an error  $< 10\%$  for the determination of BPA (see Table 1 for data generated). The results suggested that a 100-fold concentration of hydroquinone, phenol, 4-octylphenol pyrocatechol, dopamine, and ascorbic acid has no significant influence on the signals of  $2 \mu\text{M}$  BPA. Likewise, some inorganic ions such as 100-fold concentrations of  $K^+$ ,  $Zn^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$  were tested with no significant change in the BPA signal and the results are presented in Table 1.

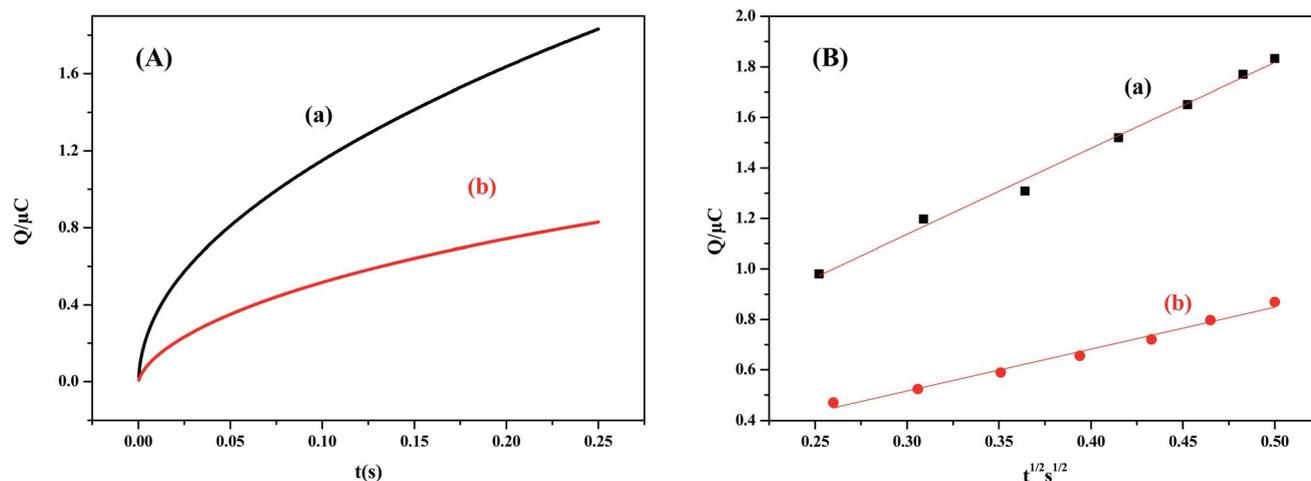


Fig. 5 (A)  $Q-t$  plot for (a) bare CPE and (b) CPE/CoPC-PAA in  $0.1 \text{ M K}_3[\text{Fe}(\text{CN})_6]$  containing  $1.0 \text{ M KCl}$ . (B)  $Q$  vs.  $t^{1/2}$  for bare CPE and a modified electrode. ( $t = 30 \text{ s}$ ,  $\text{pH } 7.2$ ; scan rate  $100 \text{ mV s}^{-1}$ ).

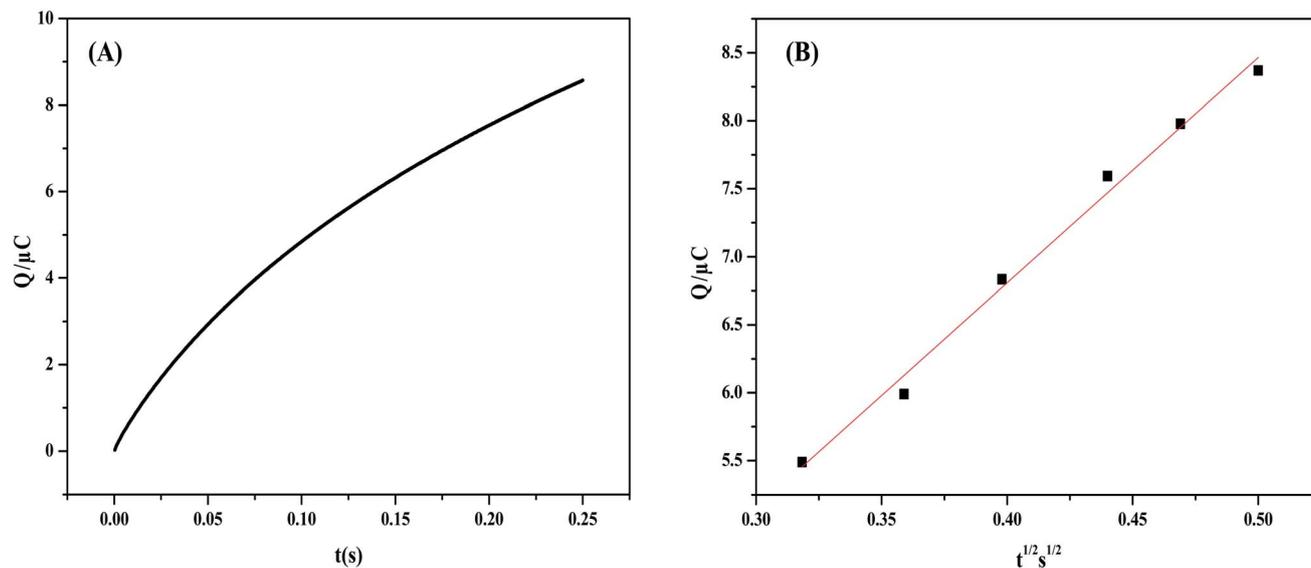


Fig. 6 (A)  $Q-t$  response for  $2.5 \mu\text{M}$  BPA at CoPc-PAA/CPE. (B) Corresponding  $Q-t^{1/2}$ . ( $t = 30 \text{ s}$ , pH 7.6; scan rate  $100 \text{ mV s}^{-1}$ ).

**Table 1** Influence of interferences on the response to  $2 \mu\text{M}$  BPA (pH 7.2; scan rate  $100 \text{ mV s}^{-1}$ ) with concentration ratio 100 : 1 ( $200 \mu\text{M}$ )

Interferents	$I_p$ ( $\mu\text{A}$ )	$\Delta I_p$ ( $\mu\text{A}$ )	Peak change for BPA signal (%)
BPA	9.65	0	0
Hydroquinone	10.14	0.49	+5.1
Phenol	10.06	0.41	+4.32
4-Octylphenol	9.89	0.24	+2.56
Pyrocatechol	9.24	-0.36	-3.78
Dopamine	9.2	-0.45	-4.7
Ascorbic acid	10	0.34	-3.6
$\text{Ca}^{2+}$	9.38	-0.27	-2.89
$\text{K}^+$	9.4	0.19	+2.03
$\text{Zn}^{2+}$	9.44	-0.21	-2.21
$\text{Na}^+$	9.76	0.11	+1.12

Based on these results, the electrochemical measurement of BPA using the CoPc-modified carbon paste electrode proved highly selective.

### 3.7. Calibration curve, linear range, and detection limit

Under the optimized experimental conditions and as shown in Fig. 7, a linear relationship between the peak current and BPA concentration was obtained from  $2.5 \times 10^{-6}$  to  $2.5 \times 10^{-11}$  M and detection limit based on the standard deviation of the blank and the slope.<sup>57</sup> The limit of detection (LOD) was 63.5 pM based on the following expression.

$$\text{LOD} = \frac{3 \times \text{Standard deviation of blank}}{\text{slope of the calibration curve}} \quad (5)$$

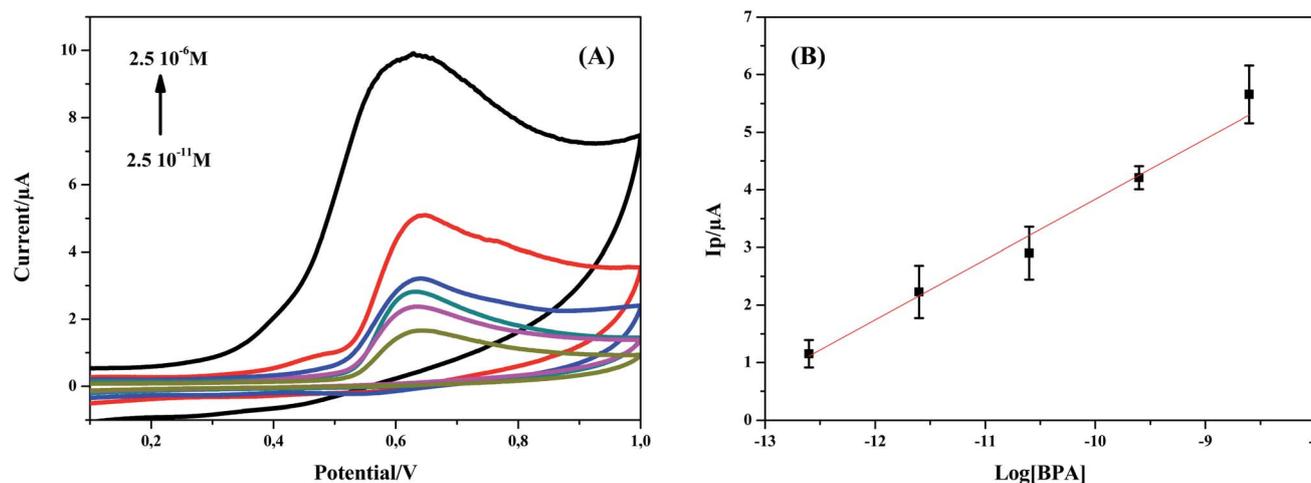


Fig. 7 (A) Cyclic voltammetry for different concentrations of BPA over the range  $2.5 \times 10^{-7}$  to  $25 \times 10^{-11}$  M, 0.1 M buffer solution (20% acetonitrile, pH 7.2) at a CoPc-PAA/CPE. (B) Calibration curve from  $25 \times 10^{-11}$  M to  $2.5 \times 10^{-7}$  M BPA ( $n = 3$ ).

**Table 2** Comparison of the analytical performances of the proposed sensor for BPA detection with other sensors from literature with similar configurations

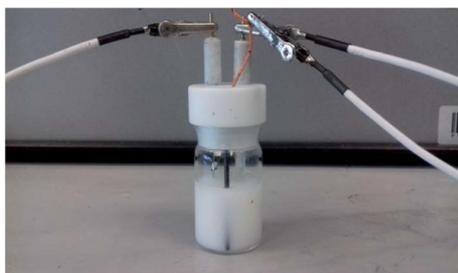
Electrode configuration	Linear range/ $\mu\text{M}$	LOD <sup>a</sup> (nM)	Ref.	Year
CTAB/CPE <sup>b</sup>	0.025–1	7.5	58	2005
MCM-41/CPE <sup>c</sup>	0.088–0.22	38	59	2009
$\beta$ -CD/IL CPE <sup>d</sup>	0.1–11	83	60	2013
Carbon nanofibers/CPE	5–400	550	61	2016
CdO/NP/IL/CPE <sup>e</sup>	0.3–40	100	62	2016
	40–650			
CdO/NPs-MOITFB-CPE <sup>f</sup>	0.01–280	1	63	2020
$\alpha$ -MoO <sub>3</sub> /CPE <sup>g</sup>	0.03–1.6	15	64	2020
[Cd(TMPP)]/CPE <sup>h</sup>	$1.5 \times 10^{-3}$ to 15	$13.5 \times 10^{-3}$	25	2020
TiO <sub>2</sub> NRs/CPE <sup>i</sup>	600–10 000	80	65	2020
FeNi <sub>3</sub> /CuS/BiOCl/CPE <sup>j</sup>	0.1–300	50	66	2021
CoPc-PAA/CPE	$25 \times 10^{-5}$ to 0.25	$63.5 \times 10^{-3}$	This work	

<sup>a</sup> LOD: limit of detection. <sup>b</sup> CTAB: cetrimonium bromide. <sup>c</sup> MCM-41: mesoporous silica molecular sieves. <sup>d</sup>  $\beta$ -CD/IL:  $\beta$ -cyclodextrin ( $\beta$ -CD) modified ionic liquid. <sup>e</sup> CdO/NP/IL: cadmium oxide nanoparticle ionic liquid. <sup>f</sup> CdO/NPs-MOITFB: cadmium oxide nanoparticle and 1-methyl-3-octylimidazolium tetrafluoroborate. <sup>g</sup>  $\alpha$ -MoO<sub>3</sub>:  $\alpha$ -molybdenum trioxide. <sup>h</sup> Cd(TMPP): 5,10,15,20-tetrakis[[4-methoxyphenyl]]porphyrinato cadmium(II) complex. <sup>i</sup> TiO<sub>2</sub> NRs: titania-nanorods. <sup>j</sup> FeNi<sub>3</sub>/CuS/BiOCl: nickel-iron copper(II) sulfide bismuth oxychloride.

A comparison of CPE/Co-Pc with other reported modified electrodes for BPA detection is listed in Table 2. The proposed method has a LOD similar to that obtained in our previous work<sup>25</sup> but with a wider linear range at low concentration ( $2.5 \times 10^{-7}$  M to  $25 \times 10^{-11}$  M) and compares favorably with other reports, as outlined in Table 2.

### 3.8. Determination of BPA in dairy samples

In order to test the applicability of the proposed electrode CPE/CoPc-PAA in a practical applications, the sensor was used for the determination of BPA in liquid milk purchased from the local market, as shown in Fig. 8. 2 mL of whole milk was added to 3 mL phosphate buffer (pH 7.2). The same sample was then

**Fig. 8** The electrochemical structure used for liquid milk analysis.**Table 3** BPA detection in milk using cyclic voltammetry at a CoPc-PAA/CPE, at pH 7.2, scan rate 100 mVs<sup>-1</sup>

Sample	Added (M)	Recovery%	RSD%
Milk	$2 \times 10^{-3}$	98.5	3.42
	$1 \times 10^{-3}$	93.7	3.25
	$1 \times 10^{-4}$	100.6	3.89
	$1 \times 10^{-5}$	102.2	4.02
	$1 \times 10^{-6}$	106.8	4.89

spiked with different amounts of BPA, namely  $2 \times 10^{-3}$  to 1  $\mu\text{M}$ , and the recoveries were in the range of 93.7–106.8%, indicating that the sensor is perfectly adequate for application in dairy samples. No BPA was found in the samples (Table 3).

## 4. Conclusion

In summary, a simple electrochemical sensor for the detection of bisphenol A was fabricated based on a carbon paste electrode modified with a derivative of cobalt phthalocyanine, C,C,C,C-tetracarboxylic acid-polyacrylamide (CoPc-PAA). The results indicated that following electrode modification, the oxidation signal of BPA was remarkably improved. The sensor preparation conditions, suitable operating conditions, calibration curve, limit of detection, and selectivity in BPA detection were presented and discussed. This new method possessed some obvious advantages, such as high determination sensitivity, a simple preparation process, rapid response and low cost. Linear range was  $25 \times 10^{-11}$  to  $2.5 \times 10^{-7}$  M with LOD at 63.5 pM. The practical application in determining BPA in milk samples was satisfactory with recovery from 93.7% to 106.8%.

## Author contributions

Dhouha Jemeli did conceptualization, methodology, validation, investigation, data curation, writing- original draft and visualization. Chérif Dridi did conceptualization, methodology, validation, writing review and editing, visualization, supervision and funding acquisition. Mohammed Nour Abbas provided CoPc molecules and its electrochemical characterisation. Eithne Dempsey did conceptualization, methodology, validation, writing review and editing, visualization and funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 E. J. Hoekstra and C. Simoneau, *Crit. Rev. Food Sci. Nutr.*, 2013, **53**, 386.
- 2 N. V. Goetz, M. Wormuth, M. Scheringer and K. Hungerbühler, *Risk Anal.*, 2010, **30**, 473.
- 3 B. S. Rubin, *J. Steroid Biochem. Mol. Biol.*, 2011, **127**, 27.
- 4 E. R. Hugo, T. D. Brandebourg, J. G. Woo, J. Loftus, J. W. Alexander and N. Ben-Jonathan, *Environ. Health Perspect.*, 2008, **116**, 1642.
- 5 M. Sugiura-Ogasawara, Y. Ozaki, S. Sonta, T. Makino and K. Suzumori, *Hum. Reprod.*, 2005, **80**, 2325.
- 6 M. Kim, Y. E. Song, J.-Q. Xiong, K.-Y. Kim, M. Jang, B.-H. Jeon and J. R. Kim, *J. Electroanal. Chem.*, 2021, **880**, 114907.
- 7 N. K. Bakirhan and S. A. Ozkan, *Safety Issues in Beverage Production*, 2020, vol. 18, p. 309.
- 8 A. Ballesteros-Gómez, S. Rubio and D. Pérez-Bendito, *J. Chromatogr. A*, 2009, **1216**, 449.
- 9 Z. Pan, F. Yu, L. Li, C. Song, J. Yang, C. Wang, Y. Pan and T. Wang, *Sep. Purif. Technol.*, 2019, **227**, 115695.
- 10 IRIS (Integrated Risk Information System), U.E.P.A. (EPA). <https://www.epa.gov/iris>.
- 11 Commission Regulation (EU) 2018/213 of 12 February 2018 on the use of bisphenol A in varnishes and coatings intended to come into contact with food and amending Regulation (EU) No 10/2011 as regards the use of that substance in plastic food contact materials (Text with EEA relevance.). <http://data.europa.eu/eli/reg/2018/213/oj>.
- 12 R. Mesa, A. Kabir, V. Samanidou and K. G. Furton, *J. Sep. Sci.*, 2019, **42**, 598.
- 13 M. Deviot, I. Lachaise, C. Högg, J. Durner, F.-X. Reichl, J.-P. Attal and E. Dursun, *Dent. Mater.*, 2018, **34**, 341.
- 14 A. S. Alnaimat, M. C. Barciela-Alonso and P. Bermejo-Barrera, *Microchem. J.*, 2019, **147**, 598.
- 15 C. Peng, N. Pan, Z. Xie, L. Liu, J. Xiang and C. Liu, *Anal. Lett.*, 2016, **49**, 1492.
- 16 M. Y. Ali, A. U. Alam and M. M. R. Howlader, *Sens. Actuators, B*, 2020, **320**, 128319.
- 17 Y. Li, H. Wang, B. Yan and H. Zhang, *J. Electroanal. Chem.*, 2017, **805**, 39.
- 18 P. A. Raymundo-Pereira, N. O. Gomes, J. H. S. Carvalho, S. A. S. Machado, O. N. Oliveira Jr. and B. C. Janegitz, *ChemElectroChem*, 2020, **7**, 3074.
- 19 O. Carr, P. A. Raymundo-Pereira, F. M. Shimizu, B. P. Sorroche, M. E. Melendez, R. de O. Pedro, P. B. Miranda, A. L. Carvalho, R. M. Reis, L. M. R. B. Arantes and O. N. Oliveira Jr, *Talanta*, 2020, **210**, 120609.
- 20 N. B. Messaoud, A. A. Lahcen, C. Dridi and A. Amine, *Sens. Actuators, B*, 2018, **276**, 304.
- 21 S. Jebri, L. Cubillana-Aguilera, J. M. Palacios-Santander and C. Dridi, *Mater. Sci. Eng., B*, 2021, **264**, 114951.
- 22 E.-y. Joa and J.-h. Lee, *Microchem. J.*, 2020, **155**, 104693.
- 23 D. Jemmeli, E. Marcoccio, D. Moscone, C. Dridi and F. Arduini, *Talanta*, 2020, **216**, 120924.
- 24 N. B. Messaoud, M. E. Ghica, C. Dridi, M. B. Ali and C. M. A. Brett, *Talanta*, 2018, **184**, 388.
- 25 D. Jemmeli, C. Mchiri, C. Dridi, H. Nasri and E. Dempsey, *RSC Adv.*, 2020, **10**, 31740.
- 26 R. Shi, J. Liang, Z. Zhao, Y. Liu and A. Liu, *Sensors*, 2018, **18**, 1660.
- 27 B. Su, H. Shao, N. Li, X. Chen, Z. Cai and X. Chen, *Talanta*, 2017, **166**, 126.
- 28 J. Huang, X. Zhang, S. Liu, Q. Lin, X. He, X. Xing and W. Lian, *J. Appl. Electrochem.*, 2011, **41**, 1323.
- 29 L. Jiang, I. Santiago and J. Foord, *Carbon*, 2021, **174**, 390.
- 30 A. U. Alam and M. J. Deen, *Anal. Chem.*, 2020, **92**, 5532.
- 31 V. N. Nemykin and E. A. Lukyanets, *ARKIVOC*, 2010, **1**, 136–208.
- 32 K. Sakamoto and E. O-Okumura, *Mater. Today*, 2009, **2**, 1127.
- 33 J. Han, X. Xu, X. Rao, M. Wei, D. G. Evans and X. Duana, *J. Mater. Chem.*, 2011, **21**, 2126.
- 34 J. H. Zagal, S. Griveau, K. I. Ozoemena, T. Nyokong and F. Bedioui, *J. Nanosci. Nanotechnol.*, 2009, **9**, 2201.
- 35 K. S. Lokesh, K. D. Wael and A. Adriaens, *Langmuir*, 2010, **26**, 17665.
- 36 J.-H. Yang, Y. Gao, W. Zhang, P. Tang, J. Tan, A.-H. Lu and D. Ma, *J. Phys. Chem. C*, 2013, **117**, 3785.
- 37 M. N. Abbas, A. L. A. Radwan, P. Bühlmann and M. A. A. El Ghaffar, *Am. J. Anal. Chem.*, 2011, **2**, 820.
- 38 N. Ben Messaoued, M. Braik, C. Dridi, M. Ben Ali, A. Ali and M. N. Abbas, *Sensor Lett.*, 2016, **14**, 928–937.
- 39 C. O. Chikere, E. Hobben, N. H. Faisal, P. Kong-Thoo-Lin and C. Fernandez, *Microchem. J.*, 2021, **160**, 105668.
- 40 X. Niua, W. Yanga, G. Wang, J. Ren, H. Guo and J. Gao, *Electrochim. Acta*, 2013, **98**, 167.
- 41 L. Zhang, Y.-P. Wen, Y.-Y. Yao, Z.-F. Wang, X.-M. Duan and J.-K. Xu, *Chin. Chem. Lett.*, 2014, **25**, 517.
- 42 X. C. Lu, L. Song, T. T. Ding, Y. L. Lin and C. X. Xu, *Russ. J. Electrochem.*, 2017, **53**, 366.
- 43 T. Ndlovu, O. A. Arotiba, S. Sampath, R. W. Krause and B. B. Mamba, *Sensors*, 2012, **12**, 11601.
- 44 A. Ghanam, A. A. Lahcen and A. Amine, *J. Electroanal. Chem.*, 2017, **789**, 58.
- 45 D. Talarico, F. Arduini, A. Constantino, M. D. C. D. Compagnone, D. Moscone and G. Palleschi, *Electrochem. Commun.*, 2015, **60**, 78.
- 46 T. Zhan, Y. Song, X. Li and W. Hou, *Mater. Sci. Eng., C*, 2016, **64**, 354.
- 47 Z. Zheng, Y. Du, Z. Wang, Q. Feng and C. Wang, *Analyst*, 2013, **138**, 693.
- 48 M. Malakootian, S. Hamzeh and H. Mahmoudi-Moghaddam, *Electroanalysis*, 2020, **33**, 38.
- 49 E. Laviron, *J. Electroanal. Chem. Interfacial Electrochem.*, 1974, **52**, 355–393.
- 50 J. Zhang, X. Xu and Z. Chen, *Ionics*, 2018, **24**, 2123.

- 51 Y. Zhou, L. Yang, S. Li and Y. Dang, *Sens. Actuators B Chem.*, 2017, **245**, 238.
- 52 X. Wang, Y. Shi, J. Shan, H. Zhou and M. Li, *Ionics*, 2020, **26**, 3135.
- 53 F. C. Anson, *Anal. Chem.*, 1964, **36**, 932.
- 54 A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2001, pp. 603–660.
- 55 R. N. Adams, *Electrochemistry at Solid Electrodes*, Marcel Dekker, New York, 1969.
- 56 H. Yin, L. Cui, S. Ai, H. Fan and L. Zhu, *Electrochim. Acta*, 2010, **55**, 603.
- 57 A. Shrivastava and V. B. Gupta, *Chron. Young Sci.*, 2011, **2**, 21.
- 58 W. Huang, *Bull. Korean Chem. Soc.*, 2005, **26**, 1560.
- 59 F. Wang, J. Yang and K. Wu, *Anal. Chim. Acta*, 2009, **638**, 23.
- 60 X. Yu, Y. Chen, L. Chang, L. Zhou, F. Tang and X. Wu, *Sens. Actuators, B*, 2013, **186**, 648.
- 61 N. Achargui, W. Chkairi, M. Elbasri, S. Alamiyoussi and M. Rhazi, *Int. J. Eng. Res. Appl.*, 2016, **6**(12), 23–29.
- 62 V. Arabali, M. Ebrahimi, S. Gheibi, F. Khaleghi, M. Bijad, A. Rudbaraki, M. Abbasghorbani and M. R. Ganjali, *Food Anal. Methods*, 2016, **9**, 1763.
- 63 F. Mehri-Talarposhti, A. G.-H. Saraei, H. Karimi-Maleh, L. Golestan and S.-A. Shahidi, *Int. J. Electrochem. Sci.*, 2020, **15**, 1904.
- 64 C. Antoniazzi, C. A. de Lima, R. Marangoni, E. G. de Castro, E. R. Santana and A. Spinelli, *Microchem. J.*, 2020, **159**, 105528.
- 65 G. Fadillah, S. Triana, U. Chasanah and T. A. Saleh, *Sens. Bio-Sens. Res.*, 2020, **30**, 100391.
- 66 M. Malakootian, S. Hamzeh and H. Mahmoudi-Moghaddam, *Electroanalysis*, 2021, **33**, 38.