Electrochemical Sensing of Bisphenol using Multilayer Graphene Nanobelts Modified Photolithography Patterned Platinum Electrode

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**Abstract**

An electrochemical sensor has been developed for the detection of BPA using photolithographically patterned platinum electrodes modified with multilayer graphene nanobelts (GNB). Compared to bare electrodes, the GNB modified electrode exhibited enhanced BPA oxidation current, due to the high effective surface area and high adsorption capacity of the GNB. The sensor showed a linear response over the concentration range from 0.5 M – 9 M with a very low limit of detection = 37.33 nM. In addition, the sensor showed very good stability and reproducibility with good specificity, demonstrating that GNB is a potential new material for the development of a practical BPA electrochemical sensor with application in both industrial and plastic industries.

Keywords**:**  multilayer graphene, bisphenol, nanobelts, electrochemical sensor, edge effects

**1. INTRODUCTION**

Bisphenol-A (BPA), a well-known estrogenic monomer which is extensively used as a raw material in plastic industries. Products like polyacrylates, epoxy resins, polyesters, and polycarbonate plastics are mainly produced from BPA. Among these, polycarbonate plastics are widely used to produce various consumer goods like baby cups and water bottles, eye glasses and plastic food containers because of its strength and hardness, excellent transparency and high resistance to acids and harsh detergents[1]. However, washing of these plastic materials with high-temperature liquids or with acidic solutions can release BPA molecules from the plastics into the environment. Abrasion and degradation of the plastic has similar consequences. The release of BPA pollutes the environment and causes severe health problems such as sexual disorders, type 2 diabetes and cancers due to hormonal disorders[2–5]. BPA can easily affect the endocrine systems in both animals and human beings[6]. It has been reported that excess leaching of BPA advances puberty[7]. Hence, it is very important to develop a sensor capable of detecting trace levels of BPA with high sensitivity and specificity.

A variety of sensing techniques including fluorescence, optical, high performance liquid chromatography, gas chromatography and surface plasmon resonance have been investigated to detect and measure BPA[8–11]. Although, these techniques are employed in BPA sensing, limitations such as their bulkiness, time consuming sampling and special conditions for operation make them unsuitable for the rapid monitoring of BPA. On the other hand, electrochemical methods find specific interest in BPA sensing because of low cost, high sensitivity and selectivity, low detection limit, fast response and portability. Electrochemical sensors so far developed to detect BPA employed various nanostructured materials like gold nanoparticles, various metal oxides, conducting polymers and carbon nanotubes[12–15]. Although, numerous studies have been reported on electrochemical sensing of BPA, there remains a challenge to develop a highly sensitive sensor for the detection of BPA with low detection limit.

Graphene has attracted wide attention over the past few years since its discovery in 2004, and many articles and books review the application of graphene in various sectors such as chemical sensors, electrochemical energy storage, catalysis, fuel cells, and batteries because of its outstanding physical and chemical properties[16–20]. Extensive efforts have been made to exploit the potential of graphene in various technological fields especially in electrochemical sensors [21–26]. Recently, novel nanostructures of graphene including nanobelts, nanoflakes, nanoribbons and nanodots are emerging as interesting alternatives to conventional graphene material [27–30]. Compared to pristine graphene and single exfoliated graphene nanosheets, these novel graphene nanostructures show a large number of edge plane defects with a high surface to volume ratio and faster electron transport property. Yuan *et al.* recently studied the comparative electrochemical performance of basal and edge plane defects in graphene samples and found that graphene samples with edge plane defects show enhanced electron transport property and high electrocatalytic activity than that of basal plane samples[31]. Although, graphene samples with edge plane defects are highly electroactive material, their application to electrochemical sensing is scarcely reported.

Therefore, the aim of this study is to develop a highly sensitive electrochemical sensor for the detection of BPA using multilayer graphene nanobelts (GNBs). For the construction of a prototype sensor device, platinum electrodes comprising reference, working and counter were lithographically patterned on a glass substrate. The results indicate that compared to bare Pt, GNB modified Pt exhibits superior catalytic activity towards the electrochemical oxidation of BPA with high sensitivity and selectivity. The limit of detection was found to be superior to other carbon nanomaterial based BPA sensors.

**2. EXPERIMENTAL**

**2.1. Synthesis of Graphene Nanobelts (GNBs)**

A suspension of graphene nanobelts in isopropanol was obtained from Nacional de Grafite, Brazil (Product name: Graphite flakes) and used as received. GNBs were prepared from natural graphite by using the chemically assisted liquid phase exfoliation method, and the detailed procedure has been reported elsewhere[32,33]. Before use, the required amount of suspension was dispersed in 100 ml of isopropanol (1 mg/mL) for 2 h using an ultrasonic bath and subsequently dried in an incubator for further use.

**2.2. Characterization Techniques and Electrochemical Measurements**

The surface morphology of the GNB samples were analysed by Field-Emission Scanning Electron Microscopy (FESEM) MERLIN Compact with GEMINI I electron column, Zeiss Pvt. Ltd., Germany). Raman spectra were in confocal configuration (NT-MDT NTEGRA Spectra, with 473 nm laser source). All the electrochemical measurements were performed using Palmsens 3 potentiostat/galvanostat instrument. All experiments were performed at room temperature with 0.1 M phosphate buffer solution (PBS), pH = 7 as the supporting electrolyte. Square Wave Voltammetry (SWV) measurement was recorded in the potential range between +0.2 V and 0.7 V with the following parameters: pulse amplitude = 0.02 V, step-potential = 0.005V, frequency = 15 Hz in 0.1 M PBS (pH 7) solution.

**2.3. Preparation of Electrodes**

For the electrochemical measurements, platinum electrodes comprising reference, working and counter were fabricated on a glass substrate using photolithography. A schematic representation of the fabrication process is shown in figure S1 in ESI, along with a photograph of the device in figure 1a. After fabrication, the as-prepared electrodes were sonicated in ethanol for 10 min in order to clean their surface. For the preparation of an in-situ Ag/AgCl reference electrode, silver was electrodeposited onto the Pt electrode using chronoamperometry (applied potential = +0.6V, time = 300 s) by immersing the electrode in silver nitrate solution. The as-prepared silver electrode was then immersed in 0.1M KCl solution and a constant potential of +0.3 V applied for 500 s. Figure 1 a shows the optical image of platinum electrode prepared by photolithography technique. A high magnification optical image of photolithography patterned electrode is shown in figure 1b, Deposition of the GNB was performed by first cleaning the surface of the working electrode with ethanol. GNB were dispersed by sonication in ethanol (2 mg/ mL) for 30 min, then, 0.5 µL of the GNB dispersion was drop cast onto the Pt and dried at room temperature. Figure 1 c and d show high and low magnification images of the platinum electrode after modification with graphene nanobelts.

**3. RESULTS AND DISCUSSION**

**3.1. Morphological and Raman Characterization of GNB**

Figure 1e and f show the FESEM images of GNB at low and high magnification. The images show a number of thin flakes of graphene with different dimensions. As can be seen, all the graphene samples show sharp edges with wrinkled morphology. The presence of these edges GNB may increase the electron transfer rate which could improve the electrochemical interfacial properties between the electrode and electrolyte[34]. Figure 1e shows the Raman spectra of GNB. The spectrum shows three prominent peaks *viz.* D band (1357 cm-1), 1581 cm-1 (G band) and 2720 cm-1 (2D band). From the intensity of the G and 2D peaks, the value of I2D/IG was calculated as 0.46, suggesting that GNB consists of multilayers of graphene[35]



**(E)**

**(F)**

**(G)**

**(A)**

**(B)**

**(C)**

**(D)**

**Figure 1.** (A) Photograph of photolithography patterned Pt electrode. Optical micrograph of (B) Patterned three electrodes (C, D) GNB modified Pt electrode surface and its closed view. Scanning electron micrograph of GNB samples (E) lower magnification (F) higher magnification (G) Raman spectra of GNB sample measured by using 473 nm laser.

**3.2. Electrochemical Characterization of GNB/Pt**

The electrochemical property of the modified electrode was investigated using K3[Fe(CN)]6 as a redox probe. Figure 2A shows CV data of a bare and GNB modified Pt electrode in 5mM K3[Fe(CN)]6 with 0.1M KCl at a scan rate of 50 mV s-1. Bare Pt shows a well-defined redox couple with the peak-to-peak separation voltage (∆Ep) of 122 mV. However, when the electrode is modified with GNB, an increase in redox current is observed with a ∆Ep value of 67 mV. The decrease in ∆Ep value with increase in redox current has been ascribed to the high electrical conductivity and large surface area of GNB, thus it enhances electron transfer rate.

The electron transfer property of the GNB modified electrode was analysed by electrochemical impedance spectroscopy. Figure 2B shows Nyquists plots of bare and GNB modified Pt electrode measured in 5 mM K3[Fe(CN)]6 solution containing 0.1 M KCl. Both plots show a straight line over the measured frequency range, indicating a diffusion limited electrochemical reaction. Equivalent circuit modelling was performed to extract electrical parameters from the data. The inset in figure 2B shows the electrical circuit, which consists of the solution resistance (RS) connected in series to a parallel combination of the double layer capacitance (C) with charge transfer resistance (Rct) and Warburg impedance (W). The overall relative deviation value of the fitting was < 2% and the values are shown in Table S1 (ESI). The value of Rct determines the electron transfer kinetics of the redox probe at the electrode/electrolyte interface. From the fit, Rct for GNB/Pt was estimated to be 17 Ω which is much lower than bare Pt (46 Ω). These results suggest that after modification of the Pt electrode by GNB, the electron transfer processes between the electrode and electrolyte interface is significantly enhanced.



**(A)**

**(B)**



**Figure 2.** (A) CVs of (a) bare Pt and (b) GNB/Pt measured in 0.1 M KCl solution containing 5 mM potassium ferrocyanide at a scan rate of 50 mV s-1. (B) Nyquist plots of (a) bare Pt and (b) GNB/Pt measured in 0.1 M KCl solution containing 5 mM potassium ferrocyanide. Inset shows the equivalent circuit.

**3.3. Electrochemical Sensing of Bisphenol**

The electrochemical sensing of BPA was analysed by cyclic voltammetry (CV)**.** Figure 3A shows CV data for bare and GNB modified Pt in the presence and absence of 0.4 mM BPA (in 0.1M PBS, pH 7) recorded at a scan rate of 50 mV s-1. All measurements were performed in the potential range of 0 to 0.8 V. In the absence of BPA, GNB/Pt showed negligible increase in current compared to the bare electrode, attributed to the high surface area and high electrical conductivity of GNB. After addition of 0.4 mM BPA, the bare Pt electrode exhibited a broad oxidation peak at 0.6 V with a very small current (Ipa = 4.5 A) indicating that electron transfer of BPA is very slow on the electrode surface. By contrast, the GNB modified Pt showed a sharp oxidation peak at 0.43 V with an enhanced peak current (Ipa = 13.2 A) suggesting that GNB greatly facilitates electron transfer. In addition, GNB/Pt showed negative shift in the oxidation potential of BPA compared to bare Pt implying that GNB possesses more electrocatalytic activity towards BPA oxidation. Figure 3B shows CVs of GNB/Pt measured in different concentrations of BPA (in 0.1M PBS at a scan rate of 50 mV s-1). From the plot, it can be seen that the oxidation peak current increases with BPA concentration.

**3.4. Effect of Scan Rate**

The effect of scan rate on the electrochemical oxidation of 0.4 mM BPA in 0.1M PBS was investigated by CV and the results are shown in figure 4A. It can be observed that the oxidation peak current increases with increasing scan rate. A plot of oxidation peak current against the square root of the scan rate is shown in figure 4B. A linear fit demonstrates that the oxidation process of BPA on GNB surface is diffusion controlled. The variation of oxidation peak position voltage (Epa) with respect to the natural logarithm of scan rate (ln )



**(A)**

**(B)**

**Figure 3.** (A) CV curves of bare Pt and GNB/Pt in the absence (a,b) and presence (c,d) of 0.4 mM BPA in 0.1 M PBS (pH 7) solution. (B) CV curves of GNB/Pt at different concentrations of BPA in 0.1 M PBS with a scan rate of 50 mV s-1



**(A)**

**(B)**

**(C)**

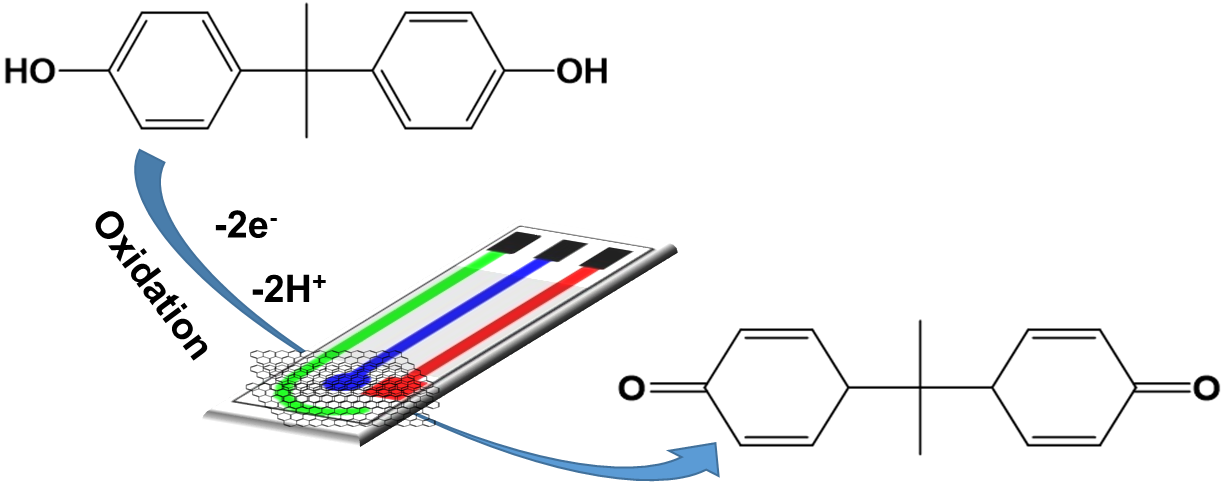
**Figure 4.** (A) CV curves of GNB/Pt in 0.1 M PBS (pH 7) solution containing 0.4mM BPA at different scan rates. (a) 20 (b) 40 (c) 60 (d) 80 (e) 100 (f) 120 (g) 150 (h) 200 (i) 300 (j) 400 (k) 500 mV s-1. (B) A plot of BPA oxidation peak current against the square root of the scan rates. Corresponding linear equation: (C) A plot between the peak potential (Epa) and natural logarithm (ln ) of the scan rates. Corresponding linear equation:

is shown in figure 4C. From the plot, a linear relationship is obtained between the two parameters Epa and ln 

For a diffusion-controlled and a totally irreversible electrochemical process, the relationship between oxidation peak voltage (Epa)and ln can be written using Laviron’s theory[36] as:

(1)

where α is the transfer coefficient, K0 is the standard rate constant of the reaction, n is the number of electrons involved in the overall electrochemical processes,  is the scan rate, E0 is the formal potential, F is the Faraday constant, R is the gas constant and T is the temperature. By equating the slope value of figure 4C with Eq. 1, the value of αn was calculated as 0.9. In general, for a totally irreversible electrochemical reaction, the value of α is assumed to be 0.5. Therefore, the value of n was estimated to be 1.8 ≈ 2. Thus, the electrochemical oxidation of BPA involves two electron and two proton transfer process which is in good agreement with previous reports[37–40]. From the above observation, a schematic representation of the reaction mechanism of BPA oxidation on GNB/Pt is illustrated in Scheme 1.

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**Scheme 1.** Schematic of BPA oxidation mechanism at GNB/Pt

**3.5.** **Determination of Effective Surface Area and Adsorption Capacity**

The effective surface area of bare Pt and GNB/Pt were determined by chronocoulometry measurements using K3[Fe(CN)]6 as a model complex. The corresponding data are shown in figure 5A. Inset of figure 5A shows the plot of charge (Q) *vs* the square root of time. The effective surface area of bare and GNB/Pt can be calculated according to Anson *et al,* using the following equation[41]

(2)

where Qdl is the double layer charge which can be eliminated by background subtraction, Qads is the Faradic charge, F is the Faraday constant (96485 A /mol), n is the number of electrons transferred, A is the effective surface area of the electrode in cm2, D is the diffusion coefficient of K3[Fe(CN)]6 (7.6 × 10-6 cm2 s-1) and C is the concentration of K3[Fe(CN)]6  solution (5 × 106 mol/cm3). The linear regression equations extracted from the inset plots of figure 5A are

Q = 35.145 × 10-6 [t1/2] – 117.148 (3)

Q = 75.493 × 10-6 [t1/2] – 193.946 (4)

By comparing the slope values of Eqns. 3 and 4 with Eqn. 2, the effective surface areas of bare and GNB/Pt were found to be 0.024 cm2 and 0.051 cm2 respectively. These results indicate that after modification of Pt electrode by GNB, the effective surface area is increased about 2 times which could significantly increase the adsorption of BPA onto the electrode surface, leading to an enhanced current response.

The chronocoulometry experiments were also carried out in the presence and absence of 0.2mM BPA in order to determine the diffusion coefficient (D) and adsorption capacity (Γs). Figure 5B shows the Q *vs* t plots of bare and GNB/Pt measured in 0.1 M PBS



**(A)**

**(B)**

**Figure 5.** (A) Plot of Q–t curve of (a) bare Pt and (b) GNB/Pt in 5 mM potassium ferrocyanide solution containing 0.1M KCl. (B) Plot of Q–t curve of GNB/Pt in the absence (a) and presence of 0.2 mM BPA in 0.1 M PBS (pH 7). Insets: Plots of Q vs t1/2 for (a) bare Pt (b) GNB/Pt.

containing 0.2 mM of BPA. Inset of figure 5B shows the plot of Q *vs*. t1/2. The linear regression equation for the two electrodes is

Q = 0.7813 [t1/2] - 1.597 (5)

Q = 21.509 [t1/2] - 40.22 (6)

From the values of the slope in Eqns.5 and 6, D was calculated to be 5.64 × 10-7 cm2 s-1 for bare Pt. This increases to 9.91 × 10-5 cm2 s-1 for GNB/Pt showing that the electron transfer rate is highly accelerated due to the presence of highly conductive GNB on the Pt surface.

The adsorption capacity (Γs) of bare and GNB modified Pt was calculated from equation (7)

(7)

where Qads is the Faradic charge due to the oxidation of adsorbed BPA, A is the effective surface area of the electrode (0.051 cm2). Thus, the adsorption capacity can be calculated as 3.45 × 10-10 mol/cm2 and 4.17 × 10-9 mol/cm2 for bare and GNB/Pt respectively. From the results, it can be seen that the adsorption capacity is increased by one order of magnitude after modification of the Pt electrode by GNB, due to the large surface to volume ratio.

**3.6. Square Wave Voltammetry Measurements**

Square wave voltammetry (SQW) was applied to measure different concentrations of BPA. Figure 6A shows the typical SQW curve of GNB/Pt measured with BPA concentrations between 0.5 M to 40 M, showing that the oxidation peak current increases with increasing concentration of BPA. A plot of oxidation peak current against BPA concentration (figure 6B) has two linear segments over the measured concentration range. The first linear fit is over the concentration range from 0.5 M to 9 M, with I (A) = 0.52[BPA] +6.43 (R2 = 0.99). Over the concentration range from 9 M to 40 M a second fit gives I (A) = 0.11[BPA] +10.33 (R2 = 0.98). From the data, the limit of detection (LOD) and limit of quantification (LOQ) of the GNB/Pt sensor can be estimated in the usual way[42]

(8)

(9)

where  is the standard deviation (determined from five measurements of the blank signal, 0.00647 µA), and *m i*s the slope extracted from the calibration plot. The calculated LOD and LOQ of the GNB/Pt BPA sensor are shown in Table 1.

Table 1 also compares the GNB/Pt sensor with the other reported BPA sensors based on different nanomaterials. As can be seen, the GNB/PT sensor shows better sensitivity and range, with good LOD compared to sensors made with other nanomaterials.

**3.7. Interference studies**

The selectivity of GNB/Pt towards BPA was investigated in the presence of several interfering species. Different concentration of interferents were added to 0.1M PBS (pH7) containing 10 M BPA and the resulting solutions were analysed using the SQW technique. The results are summarised in Table 2. The percentage variation in the peak current value can be calculated from:

(10)

where Ipc(interferents) is the cathodic peak current of the interfering species and Ipc(BPA) is the cathodic peak current of BPA. The table shows that the current is increased by between 1.8% to 15 % depending upon the interfering species. The observed selectivity phenomenon may be attributed to the fact that the addition of interfering species does not affect the oxidation of bisphenol. In other words, we can say that the oxidation potential of bisphenol at GNB surface is not matched well with the oxidation potential of other interfering species. Similar observation on the effect of interfering species on the oxidation of bisphenol has been reported by Yang *et al.* [43] and it supports the possible mechanisms involved for the high selectivity nature towards bisphenol detection in the presence of other interferants.



**(B)**



**(A)**



**Figure 6. (**A) SQW curve of GNB/Pt in 0.1 M PBS (pH7.0) containing different concentrations of BPA (a) 0 M (b) 0.5 M (c) 1 M (d) 2 M (e) 3 M (f) 4 M (g) 5 M (h) 6 M (i) 7 M (j) 8 M (k) 9 M (l) 10 M (m) 20 M (n) 30 M (o) 40 M. (B) Plot of peak current against the concentrations of BPA. Inset is the calibration plot in the concentration range – 0.5 to 9 M.

**Table 1** Comparison of the performance of GNB/Pt with the other reported BPA sensors

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Electrode | Linear range | Sensitivity  (A M-1 cm-2) | LOD  (nM) | Ref. |
| Graphene/GCE | 0.05 -  | - | 46.89 | [37] |
| Ionic liquids/graphene oxide nanosheets | 0.09 - 250 | - | 55.00 | [44] |
| Screen printed carbon electrode | 1 - 10 | - | 51.00 | [45] |
| Platinum-Graphene-Carbon nanotube/GCE | 0.06 - 10 | - | 42.00 | [46] |
| Carbon nanohorn/GCE | 2-1000 | - | 1800 | [47] |
| GNB/Pt | 0.5 - 9  9 - 40 | 7.43  1.57 | 37.33 | Present work |

**Table 2.** Effect of interferants on the determination of BPA at GNB/Pt

|  |  |  |  |
| --- | --- | --- | --- |
| S. No. | Interferents | Concentration Added  (µM) | Variation in Ipc  (%) |
| 1 | 2-chlorophenol | 10 | 9.41 |
| 2 | 3-chlorophenol | 10 | 9.81 |
| 3 | 4-chlorophenol | 10 | 9.50 |
| 4 | 2-nitrophenol | 10 | 15.25 |
| 5 | 3-nitrophenol | 10 | 9.81 |
| 6 | 4-nitrophenol | 10 | 3.90 |
| 7 | Phenol | 10 | 9.46 |
| 8 | Na+ | 100 | 3.09 |
| 9 | K+ | 100 | 1.84 |
| 10 | Zn+ | 100 | 7.61 |
| 11 | SO42- | 100 | -13.22 |
| 12 | CO32- | 100 | -13.14 |

**3.8. Repeatability and reproducibility**

The repeatability of GNB/Pt electrode was tested by performing five successive CV measurements in 0.1M PBS containing 0.4 mM BPA at a scan-rate of 50 mV s-1. Further, reproducibility of the electrode was ascertained by measuring CV for seven individual samples prepared under identical conditions. The sensor showed reproducible current value with a relative standard deviation (RSD) of 4 % for seven individual measurements and a repeatability of 3.8 % for five successive measurements. Thus, the developed GNB/Pt based BPA sensor shows good repeatability and reproducibility. In order to estimate the storage stability of GNB/Pt, the fabricated electrode was stored for two weeks and then it was tested by using CV. The electrode shows 93% of its initial response was obtained using the 0.4 mM BPA suggested the good stability of the prepared electrode.

**3.9. Real Time Analysis**

In order to analyse the applicability of the developed BPA sensor in real time analysis, the GNB/Pt electrode was used to detect BPA in tap water samples using standard addition methods. Table S2 in ESI shows the respective data obtained in the determination of BPA in water sample. From the data, it has been inferred that nearly 90% recovery is obtained with the RSD value of 1.6%.

**4. CONCLUSIONS**

A highly sensitive electrochemical BPA sensor was developed using GNB modified photolithography patterned platinum electrodes. SEM and RAMAN data confirm the presence of edge effects which enhance the electrocatalytic activity of the electrode towards BPA. GNB modified Pt shows enhanced BPA oxidation current compared to bare electrode, attributed to its high effective surface area and adsorption capacity. In addition to high sensitivity, the sensor has high stability and reproducibility with good specificity, demonstrating that GNB is a potential material for making practical electrochemical BPA sensors.

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**REFERENCES**

[1] Vogel S A 2009 The politics of plastics: the making and unmaking of bisphenol a “safety” *Am. J. Public Health* **99** S559–66

[2] Li D, Zhou Z, Qing D, He Y, Wu T, Miao M, Wang J, Weng X, Ferber J R and Herrinton L J 2009 Occupational exposure to bisphenol-A (BPA) and the risk of self-reported male sexual dysfunction *Hum. Reprod.* dep381

[3] Silver M K, Sowers M R and Park S K 2011 Urinary bisphenol A and type-2 diabetes in US adults: data from NHANES 2003–2008 *PLoS One* **6** e26868

[4] Jenkins S, Raghuraman N, Eltoum I, Carpenter M, Russo J and Lamartiniere C A 2009 Oral exposure to bisphenol A increases dimethylbenzanthracene-induced mammary cancer in rats *Env. Heal. Perspect* **117** 910–5

[5] Dairkee S H, Seok J, Champion S, Sayeed A, Mindrinos M, Xiao W, Davis R W and Goodson W H 2008 Bisphenol A induces a profile of tumor aggressiveness in high-risk cells from breast cancer patients *Cancer Res.* **68** 2076–80

[6] Maffini M V, Rubin B S, Sonnenschein C and Soto A M 2006 Endocrine disruptors and reproductive health : The case of bisphenol-A *Mol. Cell. Endocrinol.* **255** 179–86

[7] Howdeshell K L, Hotchkiss A K, Thayer K A, Vandenbergh J G and vom Saal F S 1999 Environmental toxins: Exposure to bisphenol A advances puberty *Nature* **401** 763–4

[8] Wang X, Zeng H, Wei Y and Lin J-M 2006 A reversible fluorescence sensor based on insoluble β-cyclodextrin polymer for direct determination of bisphenol A (BPA) *Sensors Actuators B Chem.* **114** 565–72

[9] Inoue K, Kato K, Yoshimura Y, Makino T and Nakazawa H 2000 Determination of bisphenol A in human serum by high-performance liquid chromatography with multi-electrode electrochemical detection *J. Chromatogr. B Biomed. Sci. Appl.* **749** 17–23

[10] Chanbasha Basheer †, Anass Ali Alnedhary ‡, B. S. Madhava Rao ‡, Suresh Valliyaveettil \* † and and Hian Kee Lee\* † 2006 Development and Application of Porous Membrane-Protected Carbon Nanotube Micro-Solid-Phase Extraction Combined with Gas Chromatography/Mass Spectrometry *Anal. Chem.* **78** 2853–8

[11] Hegnerová K, Piliarik M, Šteinbachová M, Flegelová Z, Černohorská H and Homola J 2010 Detection of bisphenol A using a novel surface plasmon resonance biosensor *Anal. Bioanal. Chem.* **398** 1963–6

[12] Huang J, Zhang X, Liu S, Lin Q, He X, Xing X and Lian W 2011 Electrochemical sensor for bisphenol A detection based on molecularly imprinted polymers and gold nanoparticles *J. Appl. Electrochem.* **41** 1323–8

[13] Hou C, Tang W, Zhang C, Wang Y and Zhu N 2014 A novel and sensitive electrochemical sensor for bisphenol A determination based on carbon black supporting ferroferric oxide nanoparticles *Electrochim. Acta* **144** 324–31

[14] Poorahong S, Thammakhet C, Thavarungkul P, Limbut W, Numnuam A and Kanatharana P 2012 Amperometric sensor for detection of bisphenol A using a pencil graphite electrode modified with polyaniline nanorods and multiwalled carbon nanotubes *Microchim. Acta* **176** 91–9

[15] Moraes F C, Silva T A, Cesarino I and Machado S A S 2013 Effect of the surface organization with carbon nanotubes on the electrochemical detection of bisphenol A *Sensors Actuators B Chem.* **177** 14–8

[16] Huang X, Yin Z, Wu S, Qi X, He Q, Zhang Q, Yan Q, Boey F and Zhang H 2011 Graphene‐based materials: synthesis, characterization, properties, and applications *Small* **7** 1876–902

[17] Huang G and Chen J 2009 Synthesis and applications of graphene *Carbon Tech.* **1** 13

[18] Choi W, Lahiri I, Seelaboyina R and Kang Y S 2010 Synthesis of graphene and its applications: a review *Crit. Rev. Solid State Mater. Sci.* **35**

[19] Choi W and Lee J 2011 *Graphene: synthesis and applications* (CRC Press)

[20] Warner J H, Schaffel F, Rummeli M and Bachmatiuk A 2012 *Graphene: fundamentals and emergent applications* (Newnes)

[21] Öztürk A and Alanyalıoğlu M 2016 Electrochemical fabrication and amperometric sensor application of graphene sheets *Superlattices Microstruct.* -

[22] Lawal A T 2015 Synthesis and utilisation of graphene for fabrication of electrochemical sensors *Talanta* **131** 424–43

[23] Qi S, Zhao B, Tang H and Jiang X 2015 Determination of ascorbic acid, dopamine, and uric acid by a novel electrochemical sensor based on pristine graphene *Electrochim. Acta* **161** 395–402

[24] Er E, Celikkan H, Aksu M L and Erk N 2015 A novel and highly sensitive electrochemical sensor based on a high-quality modified graphene electrode for the determination of hydrochlorothiazide in pharmaceutical formulations and human plasma *Anal. Methods* **7** 9254–60

[25] Adhikari B-R, Govindhan M and Chen A 2015 Sensitive Detection of Acetaminophen with Graphene-Based Electrochemical Sensor *Electrochim. Acta* **162** 198–204

[26] Moraes F C, Rossi B, Donatoni M C, de Oliveira K T and Pereira E C 2015 Sensitive determination of 17β-estradiol in river water using a graphene based electrochemical sensor *Anal. Chim. Acta* **881** 37–43

[27] Jiao L, Wang X, Diankov G, Wang H and Dai H 2010 Facile synthesis of high-quality graphene nanoribbons *Nat Nano* **5** 321–5

[28] Lounasvuori M M, Rosillo-Lopez M, Salzmann C G, Caruana D J and Holt K B 2014 Electrochemical characterisation of graphene nanoflakes with functionalised edges. *Faraday Discuss.* **172** 293–310

[29] Zhu H, Xu Y, Liu A, Kong N, Shan F, Yang W, Barrow C J and Liu J 2015 Graphene nanodots-encaged porous gold electrode fabricated via ion beam sputtering deposition for electrochemical analysis of heavy metal ions *Sensors Actuators B Chem.* **206** 592–600

[30] Kannan P K, Moshkalev S A and Rout C S 2016 Highly sensitive and selective electrochemical dopamine sensing properties of multilayer graphene nanobelts *Nanotechnology* **27** 75504

[31] Yuan W, Zhou Y, Li Y, Li C, Peng H, Zhang J, Liu Z, Dai L and Shi G 2013 The edge-and basal-plane-specific electrochemistry of a single-layer graphene sheet *Sci. Rep.* **3**

[32] Alaferdov A V, Gholamipour-Shirazi A, Canesqui M A, Danilov Y A and Moshkalev S A 2014 Size-controlled synthesis of graphite nanoflakes and multi-layer graphene by liquid phase exfoliation of natural graphite *Carbon* **69** 525–35

[33] Rouxinol F P, Gelamo R V, Amici R G, Vaz A R and Moshkalev S A 2010 Low contact resistivity and strain in suspended multilayer graphene *Appl. Phys. Lett.* **97** 253104

[34] Mutyala S and Mathiyarasu J 2015 Preparation of graphene nanoflakes and its application for detection of hydrazine *Sensors Actuators B Chem.* **210** 692–9

[35] Wu W, Liu Z, Jauregui L A, Yu Q, Pillai R, Cao H, Bao J, Chen Y P and Pei S 2010 Sensors and Actuators B : Chemical Wafer-scale synthesis of graphene by chemical vapor deposition and its application in hydrogen sensing *Sensors Actuators B. Chem.* **150** 296–300

[36] Laviron E 1979 General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems *J. Electroanal. Chem. Interfacial Electrochem.* **101** 19–28

[37] Ntsendwana B, Mamba B B, Sampath S and Arotiba O A 2012 Electrochemical detection of bisphenol A using graphene-modified glassy carbon electrode *Int J Electrochem Sci* **7** 3501–12

[38] Huang K-J, Liu Y-J, Liu Y-M and Wang L-L 2014 *Molybdenum disulfide nanoflower-chitosan-Au nanoparticles composites based electrochemical sensing platform for bisphenol A determination* *J. Hazar. Mater.* **276** 207-215

[39] Lin Y, Liu K, Liu C, Yin L, Kang Q, Li L and Li B 2014 Electrochemical sensing of bisphenol A based on polyglutamic acid/amino-functionalised carbon nanotubes nanocomposite *Electrochim. Acta* **133** 492–500

[40] Peng L, Dong S, Xie H, Gu G, He Z, Lu J and Huang T 2014 Sensitive simultaneous determination of diethylstilbestrol and bisphenol A based on Bi2WO6 nanoplates modified carbon paste electrode *J. Electroanal. Chem.* **726** 15–20

[41] Anson F C 1964 Evidence for Adsorption of Cobale (III)-(Ethylenedinitrilo) Tetraacetate at Platinum Electrodes. *Anal. Chem.* **36** 520–3

[42] Kannan P K and Rout C S 2015 High Performance Non-enzymatic Glucose Sensor Based on One-Step Electrodeposited Nickel Sulfide *Chem. – A Eur. J.* **21** 9355–9

[43] Yang L, Zhao H, Fan S, Li B and Li C P 2014 A highly sensitive electrochemical sensor for simultaneous determination of hydroquinone and bisphenol A based on the ultrafine Pd nanoparticle@TiO2 functionalized SiC *Anal. Chim. Acta* **852** 28–36

[44] Beitollahi H and Tajik S 2015 Construction of a nanostructure-based electrochemical sensor for voltammetric determination of bisphenol A *Environ. Monit. Assess.* **187** 1–11

[45] Brugnera M F, Trindade M A G and Zanoni M V B 2010 Detection of Bisphenol A on a Screen-Printed Carbon Electrode in CTAB Micellar Medium *Anal. Lett.* **43** 2823–36

[46] Zheng Z, Du Y, Wang Z, Feng Q and Wang C 2013 Pt/graphene-CNTs nanocomposite based electrochemical sensors for the determination of endocrine disruptor bisphenol A in thermal printing papers *Analyst* **138** 693–701

[47] Xu G, Gong L, Dai H, Li X, Zhang S, Lu S, Lin Y, Chen J, Tong Y and Chen G 2013 Electrochemical bisphenol A sensor based on carbon nanohorns *Anal. Methods* **5** 3328–33