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SENSORS and ACTUATORS B Chemical

Fabrication of highly sensitive Bisphenol A electrochemical sensor amplified with chemically modified multiwall carbon nanotubes and β-cyclodextrin

Md Younus Ali[a,b], Arif Ul Alam[a], Matiar M.R. Howlader[a,*]

[a] *Department of Electrical and Computer Engineering, McMaster University, 1280 Main Street West, Hamilton, ON, L8S 4K1, Canada*
[b] *Electronics and Communication Engineering Discipline, Khulna University, Khulna 9208, Bangladesh*

ABSTRACT

Bisphenol A (BPA), one of the most extensively used plasticizers, is an endocrine disrupting chemical (EDC). Leaching of BPA in food, and water sources causes adverse health effects, therefore, it requires monitoring. In this work, we developed a simple, low-cost electrochemical sensor for detecting a very low level of BPA in water using chemically modified multiwall carbon nanotubes (MWCNTs) with β-cyclodextrin (βCD) on screen-printed carbon electrode (SPCE). The electrochemical sensing of BPA showed a completely irreversible process with diffusion-controlled oxidation involving two electrons and two protons. At an optimized condition, the sensor showed a two-step linear response from 125 nM to 2 μM and 2 to 30 μM, with correlation coefficients of 0.997 and 0.995, respectively. The limit of detection for BPA was determined to be 13.76 nM (SNR = 3). The improved sensing performance is attributed to host-guest interaction ability of MWCNTs- βCD with BPA due to the combined effect of hydrophilic behavior of βCD and large surface area of MWCNTs. The sensors exhibited an excellent reproducibility (RSD = 4.7 %) and stable response over five weeks and negligible interference with common chemical species in water. The sensor's reliability test in lake and tap water showed an excellent recovery of BPA ranging from 96.05 %–108.70 %. These favorable results can enable the development of simple and cheap portable sensors for monitoring a wide range of BPA levels in the water.

1. Introduction

Bisphenol A (BPA) is one of the most commonly used plasticizers in plastic products, such as polycarbonate and epoxy resins worldwide [1,2]. Specifically, this low-cost raw material is prevalent for food containers, drink packaging, and beverage cans due to its high flexibility, thermal stability, toughness, and endurance. The general name of BPA is used for 2, 2-bis (4-hydroxyphenyl) propane, and its chemical formula is $(CH_3)_2C(C_6H_4OH)_2$ [1,3]. In general, BPA can be released into the environment by (1) manufacturing waste, (2) leaching, and (3) disposing of plastics [3,4]. Every year, about 2000 tons of BPA including its products are released into the environment, making water toxic and polluted, which causes adverse effects in human health [5]. European Food Safety Authority and the United States Environmental Protection Agency recommended that the maximum acceptable and tolerable daily intake of BPA is 50 μg/kg BW/day [6,7]. BPA is one of the most studied endocrine disrupting chemicals (EDCs), responsible for deceiving the endocrine system into releasing high levels of hormones such as estrogen in the body [8]. These high levels of hormones are the causes of many disorders including birth defects, infertility,

reproduction issue, metabolism problem, tumors, and other developmental and behavioral disorders [9–12]. Therefore, the detection of BPA in water is very essential for health and environment monitoring.

Different types of lab-based analytical techniques, such as liquid chromatography-mass spectrometry (LC–MS) [13–15], gas chromatography-mass spectrometry (GC–MS) [16], high-performance liquid chromatography (HPLC) [17], and ultra-performance liquid chromatography-mass spectrometry (UPLC-MS) [18] are being used to detect BPA in the environment, food and beverage. While these techniques are highly sensitive and reproducible, they are expensive, time-consuming and need skilled operators to operate the instruments. Consequently, these limitations hinder the real-time, cost-effective detection of BPA. Moreover, BPA can be detected by colorimetric methods [19], fluorescent method [20], biosensors [21–23], and molecular imprinted polymer (MIP) [24]. Although these methods are highly sensitive, MIPS and biosensors are not suitable for environmental (i.e. water) monitoring because of their complex fabrication and high-cost. These sensors are also unstable, temperature dependent, and unreliable.

Electrochemical sensing offers an alternative approach to the detection of BPA in water [25]. Electrochemical sensors promise to fast

response, lower costs, and ease-of-fabrication while allowing high sensitivity and reproducibility [26–32]. In electrochemical sensing of BPA, an irreversible process of BPA's oxidation at bare working electrode produces dimers, which foul the electrode and decrease oxidation current. Moreover, oxidation at the bare electrode requires higher potential which reduces sensors' sensitivity. To address these issues, the sensors are designed by modifying the working electrode with different materials such as carbon-based nanomaterials [33–35] and their combination with nanoparticles [36–38]. These materials show catalytic activity to BPA analyte. While many of these sensors do not provide a low limit of detection [37,39] and others do not offer low-cost or high linear range [33,40], there is a trade-off among detection limits, concentration range, selectivity and stability of the sensors for the application needs.

Carbon nanotubes (CNTs) and modified CNTs have been used as an electrochemical sensor because of their low fabrication cost, and excellent electrochemical properties [39,41–43]. For example, CNTs modified with β-cyclodextrin (βCD) exhibited high sensitivity in BPA detection because of the large effective surface area of CNTs and host-guest interaction abilities of βCD [44–47]. Physical modification of CNTs with βCD is a simple method; however, the resultant material lacks a direct electron transfer path [44] and it is unstable because βCD is soluble in water [48]. The composite of chemically (covalently) modified CNTs with βCD increases host-guest interaction abilities which shows higher sensitivity than physically modified CNTs-βCD [44]. Also, there are different approaches including "click" chemistry (CC) based- [49], and thionyl chloride-mediated esterification (TE) [44] used for chemical modification of CNTs with βCD. While the CC method is a complex and multistep (four-step) synthesis process, the TE method (two-step synthesis) provides a relatively small amount of βCD attachment at the edges of the CNTs. Besides, the TE method needs processing in controlled air as well as moisture sensitive substances.

In this work, we fabricated a simple, rapid, cheap, and highly sensitive electrochemical BPA sensor based on chemically (covalently) modified multi-walled carbon nanotubes (MWCNTs) with βCD on screen-printed carbon electrode (SPCE). The chemical modification of MWCNTs-βCD was done by one step steglich esterification [50] on the SPCE surface due to its higher immobilization of βCD with MWCNTs over CC and TE methods.

2. Materials, method and procedure

2.1. Reagents and materials

Bisphenol A (BPA), bisphenol S (BPS), acetaminophen (APAP), β-Cyclodextrin (βCD, ≥97 %), *N,N*-dimethylformamide (DMF) (>99.9 %), anhydrous *N,N*-dimethylformamide (DMF) (99.8 %), dicyclohexylcarbodiimide (DCC) (60 wt % in xylenes), 4-(dimethylamino)pyridine (DMAP) (≥99 %), potassium ferricyanide (III), phosphate buffer solution (PBS) tablets were purchased from Sigma Aldrich Canada.

MWCNTs (>95 %, OD: 5–15 nm, length: ~50 μm, electrical conductivity: >100 S·cm^{-1}), and COOH-functionalized MWCNTs (MWCNTs−COOH, >95 %, OD: 5–15 nm, length: ~50 μm, electrical conductivity: >100 S·cm^{-1}) were purchased from U.S. Research Nanomaterials Inc. All of these chemicals were of analytical grade. One PBS tablet was dissolved into 200 ml DI water to get 0.01 M phosphate buffer solutions (pH 7.4) with 0.0027 M potassium chloride and 0.137 M sodium chloride. To prepare 0.01 M phosphate buffer solutions of different pH ((pH 5.8–9.20) with 0.0027 M KCl and 0.137 M NaCl, a suitable amount of KCl, NaCl, Na$_2$HPO$_4$ and NaH$_2$PO$_4$ were dissolved into DI.

2.2. Apparatus

PalmSens EmStat 3 potentiostat with a three-electrode cell and PSTrace 4.8 software was used for all electrochemical measurements (cyclic voltammetry (CV)/linear sweep voltammetry (LSV)) at room temperature (25 ± 2 °C) where a platinum (Pt) wire was used as a counter electrode and an Ag/AgCl electrode was used as a reference electrode. The SPCE electrode (3 mm diameter i.e. exposed area of 0.071 cm^2), the counter electrode and the reference electrodes were purchased from CH Instruments Inc. USA. DI water (resistivity ≥ 18 MΩ cm), used for preparing different aqueous solutions, was purified by ELGA Purelab Ultra Water Purifier. Before each electrochemical measurement, the BPA analyte with the working electrode, was stirred by Thermo Scientific RT Basic magnetic stirrer. The water contact angle measurement of the working electrode modified with MWCNTs as well as chemically mixed MWCNTs-βCD composite was done by KRUSS DSA 100 drop shape analyzer.

2.3. Preparation of working electrode

MWCNTs of 2 mg mL^{-1} was prepared by dispersing 40 mg of MWCNTs into 20 ml DI water using a probe ultrasonic preprocessor for 10 min. Aqueous solution of MWCNTs-βCD(Chem) and MWCNTs-βCD (Phys) was obtained by following the processes used by Alam et al. [50]. The sensitivity of bare SPCE is not good. We have modified the SPCE electrode by drop-casting aqueous solution of pure MWCNTs or MWCNTs-βCD(Phys) or MWCNTs-βCD(Chem). Then, the drop-casted electrode was dried at room temperature for at least 12 h to use for BPA detection. Here, we focused on the steglich esterification process of MWCNTs-βCD because it provides superior immobilization of βCD with MWCNTs. In our previous work, we have provided the covalent linking between MWCNTs and βCD, where the characteristic peaks of ester groups in the FTIR spectra comprise the stretching vibration peak of C = O (at 1729 and 1725 cm^{-1}) and the symmetric vibration peak of −COO$^-$ (at 1382 cm^{-1}), confirming the covalent modification of MWCNT with βCD through SE chemistry [50]. The preparation of chemically modified MWCNTs-βCD (MWCNTs-βCD(Chem))/SPCE is shown in Fig. 1. The amount of MWCNTs-βCD used for modifying the
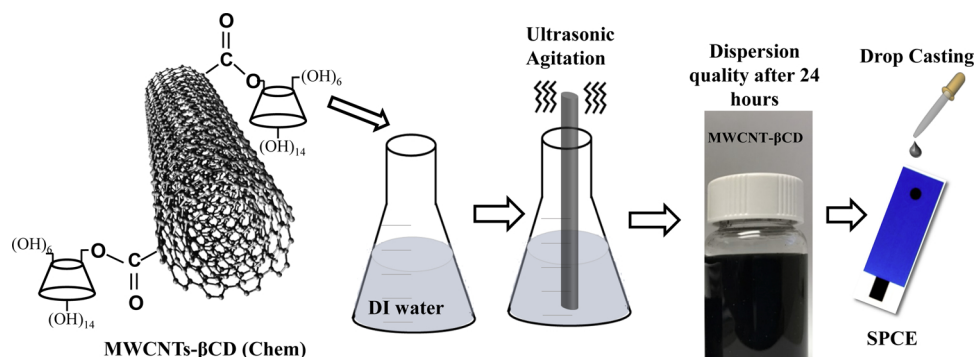

Fig. 1. Schematic of the modification of screen-printed carbon electrode with MWCNTs- βCD (Chem).

electrode played a significant role in the oxidation of BPA. We got higher oxidation current when we used 10 µl of MWCNTs-βCD as shown in Fig. SI 1. Therefore, in this work, 10 µl aqueous solution of MWCNTs and MWCNTs-βCD was used.

2.4. Preparation of real sample

BPA is a transparent solid which is soluble in organic solvents but poorly soluble in water. For this reason, first, we made a 1 mM stock solution of BPA using methanol. We prepared a PBS solution of pH 7.4 using DI water. We diluted the stock solution in PBS such that the total proportion of methanol in the solution was less than 1 %. Fig. SI 2 shows the effects of methanol level in peak oxidation current of BPA. A similar process was used to prepare the BPA sample using tap and lake water. For each electrochemical measurement, we used 50 ml of BPA aqueous solution in a glass beaker.

3. Results and discussion

3.1. Role of MWCNTs-βCD/SPCE

The electrochemical sensing of BPA relies on the redox activity of the working electrode towards BPA analyte. To compare the electrochemical sensing performance of different modified working electrodes, cyclic voltammetry (CV) was done, which is shown in Fig. 2. The sensing electrodes of MWCNTs with and without βCD showed oxidation peaks, but no reduction peaks, indicating the electrochemical sensing of BPA is an irreversible oxidation process. The scan rate and pH-dependent analysis confirmed that BPA oxidation involves 2 electrons and 2 photons as illustrated below [51].
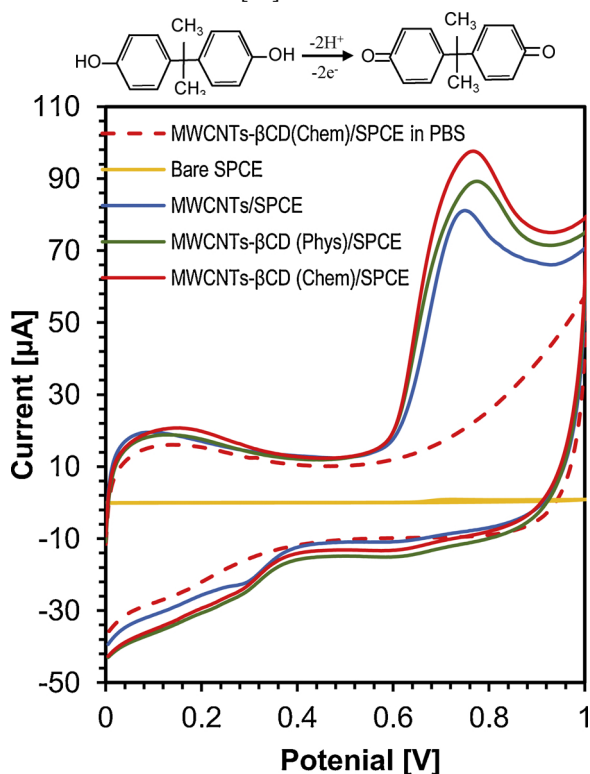
Fig. 2. CVs of MWCNTs-βCD (Chem)/ SPCE (red dashed line) in the absence of BPA in 0.01 M PBS (pH 7.4); CVs of bare SPCE (yellow), MWCNTs/SPCE (blue), MWCNTs-βCD (Phys)/SPCE (green) and MWCNTs-βCD (Chem)/ SPCE (red) in the presence of 20 µM BPA (solid lines) in 0.01 M PBS (pH 7.4) at a scan rate of 60 mV/s (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
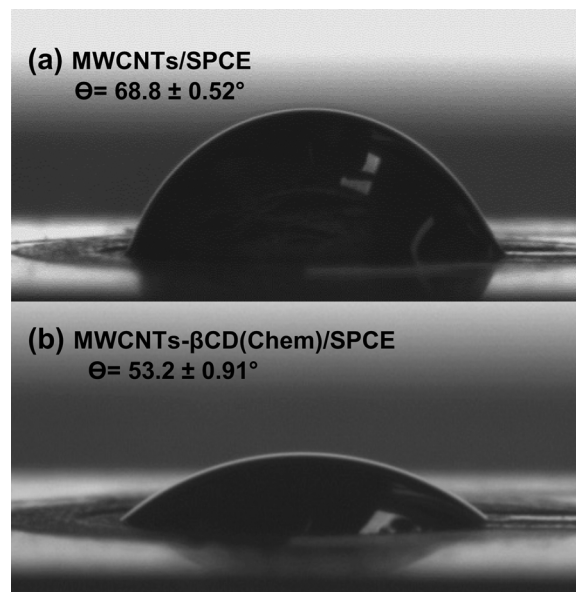
Fig. 3. Water contact angle measurement of (a) MWCNTs/SPCE and (b) chemically modified MWCNTs-βCD/SPCE working electrode.

The sensitivity of bare SPCE electrode toward BPA analyte was poor where the estimated peak oxidation current (I_{pa}) was 0.766 µA at oxidation potential (V_{pa}) of + 0.72 V. In the absence of BPA (in PBS, pH: 7.4), no oxidation was observed by MWCNTs-βCD (Chem)/SPCE electrode (red-dashed line, Fig. 2). However, the area under the CV curves was considerably increased than that of SPCE (yellow curve) due to an increase of double-layer capacitance. The MWCNT/SPCE electrode showed high I_{pa} of 68 µA around V_{pa} = + 0.72 V. As shown in Fig. 2, utilizing MWCNTs-βCD (Phys)/SPCE and MWCNTs-βCD (Chem)/SPCE electrodes further improved the oxidation peak current which was 75.51 µA and 84.88 µA, respectively at + 0.73 V. This significant enhancement of the sensitivity can be attributed to high conductivity and large surface area of MWCNTs, the porosity of βCD, and host-guest interaction capability of MWCNTs-βCD composite [52].

From Fig. 2, it is observed that MWCNTs-βCD (Chem)/SPCE outperforms other working electrodes. The enhancement in oxidation current by MWCNTs-βCD (Chem)/SPCE might be due to the multilayer surface structure of MWCNTs-βCD (Chem)/SPCE which could adsorb more BPA than that of pure MWCNTs. It is worth noting that the inner core of βCD is hydrophobic while the outer surface of βCD is hydrophilic, which is responsible for BPA adsorption. To examine the surface wettability (hydrophilicity), we investigated the water contact angle of MWCNTs/SPCE and MWCNTs-βCD (Chem)/SPCE electrodes as shown in Fig. 3. The water contact angle of MWCNTs/SPCE and MWCNTs-βCD (Chem)/SPCE electrodes was 68.8 ± 0.52° and 53.2 ± 0.91° respectively. Thus, higher hydrophilic behavior of MWCNTs-βCD/SPCE specimen than that of MWCNTs/SPCE may facilitate more oxidation of BPA and provide higher sensitivity toward BPA.

3.2. Role of surface area

$K_3[Fe(CN)_6]$ redox probe has well-known electrochemical activities and is commonly used as an internal standard for developing electrodes in aqueous solutions [53,54]. We examined the redox behaviors of different working electrodes by $K_3[Fe(CN)_6]$ redox probe. Fig. 4(a) represents the CV curves of different working electrodes in an aqueous solution of 5.0 mM $K_3[Fe(CN)_6]$ with 0.1 M KCl at a scan rate of 60 mV/s. The difference between oxidation and reduction potential (ΔE_p) was 359 mV for bare SPCE. For MWCNTs/SPCE, MWCNTs-βCD(Phys)/SPCE, and MWCNTs-βCD(Chem)/SPCE, we observed a decrease in ΔE_{pa}
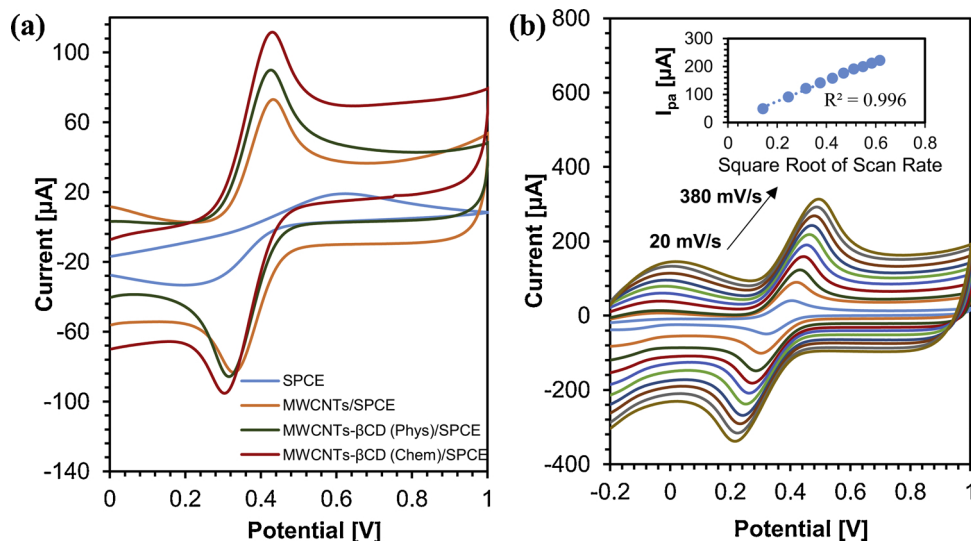
Fig. 4. (a) CV curves of different electrodes in an aqueous solution of 5.0 mM $K_3[Fe(CN_6)]$ with 0.1 M KCl at a scan rate of 60 mV/s. (b) CV curves for MWCNTs-βCD (Chem)/SPCE at different scan rate (20, 60, 100, 140, 180, 220, 260, 300, 340, and 380 mV/s) in the same solution.

and an increase in peak oxidation current (I_{pa}). Because of large surface area and high conductivity of MWCNTs, the modified electrodes provide faster electron transfer than that of bare SPCE. Fig. 4 (b) represents the CV curves of the MWCNTs-βCD (Chem)/SPCE working electrode at different scan rates. The effective surface area of the electrode can be calculated by using the Randles–Sevcik equation [53]:

$$I_p = 2.69 \times 10^5 AD^{1/2}n^{3/2}\nu^{1/2}c \tag{1}$$

Where I_p is the peak oxidation or reduction current (A), A is the effective surface area (cm^2), D (6.67×10^{-6} cm^2 s^{-1}) is the diffusion coefficient of $K_3[Fe(CN_6)]$, n is the number of electron transfer (n = 1), ν is the scan rate (V/s) and C is the bulk concentration of $K_3[Fe(CN_6)]$ (mol/cm^3).

The inset picture of Fig. 4(b) shows the square root of the scan rate vs. peak oxidation current. The units of I_{pa} and ν are ampere and V/s, respectively. The slope of the I_{pa}-$\nu^{1/2}$ curve is 0.00036 (A.s/V), which is used in Eq. (1) to calculate the effective surface area. The effective surface area of MWCNTs-βCD(Chem)/SPCE was 0.115 cm^2 which is much higher than that of MWCNTs/SPCE (0.086 cm^2) and bare SPCE (0.071 cm^2). Therefore, MWCNTs-βCD (Chem)/SPCE with larger surface area offers much higher sensitivity than other electrodes.

3.3. Effect of scan rate on BPA sensing

The number of electron transfer during the oxidation process of BPA

was examined by scan rate dependent characteristics of MWCNTs-βCD (Chem)/SPCE in PBS (pH 7.4) with 20 μM BPA. The CV results demonstrated that BPA exhibited irreversible oxidation. Thus, for simplicity and rapid sensing, linear sweep voltammetry (LSV) was used at different scan rates as shown in Fig. 5. The total oxidation current in electrochemical sensing is the sum of Faraday's current and charging current. Usually, Faraday's current is constant with scan rate while charging current increases with scan rate, thus, the oxidation current increased with scan rate. The linear regression relationship of peak oxidation current (I_{pa}) and square root of scan rate can be expressed as:

$$I_{pa}(\mu A) = -72.614 + 19.287\nu^{\frac{1}{2}} (\nu: mVs^{-1}, R^2 = 0.994) \tag{2}$$

The linear relationship between I_{pa} and $\nu^{\frac{1}{2}}$ indicates that the oxidation process was a diffusion-controlled electron transfer process. Fig. 5(c) represents the relationship between peak oxidation voltage (E_{pa}) and the natural logarithm of scan rate (ν) ($ln\nu$) which can be expressed as:

$$E_{pa}(V) = 0.538 + 0.0479ln\nu (\nu: mVs^{-1}, R^2 = 0.9814) \tag{3}$$

For an irreversible electrode process, the oxidation potential is expressed by E. Laviron equation [55]:

$$E_{pa} = E^0 + \left(\frac{RT}{\alpha nF}\right)ln\left(\frac{RTK^0}{\alpha nF}\right) + \left(\frac{RT}{\alpha nF}\right)ln\nu \tag{4}$$

Where R is the universal gas constant, T is the absolute temperature, α is the transfer coefficient, n is the number of electron transfer, F is the
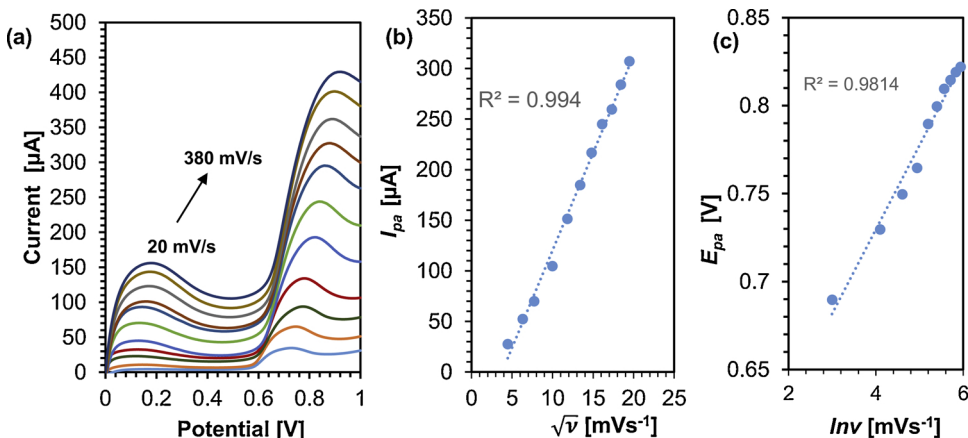

Fig. 5. (a) LSV of MWCNTs-βCD(Chem)/SPCE in 0.01 M PBS (pH 7.4) with 20 μM BPA at different scan rates (20, 60, 100, 140, 180, 220, 260, 300, 340, 380 mVs^{-1}) (b) The relationship between oxidation peak currents (I_{pa}) and square root of the scan rates, ν (mVs^{-1}) (c) The dependency of oxidation peak potential (E_{pa}) of BPA on $ln\nu$.
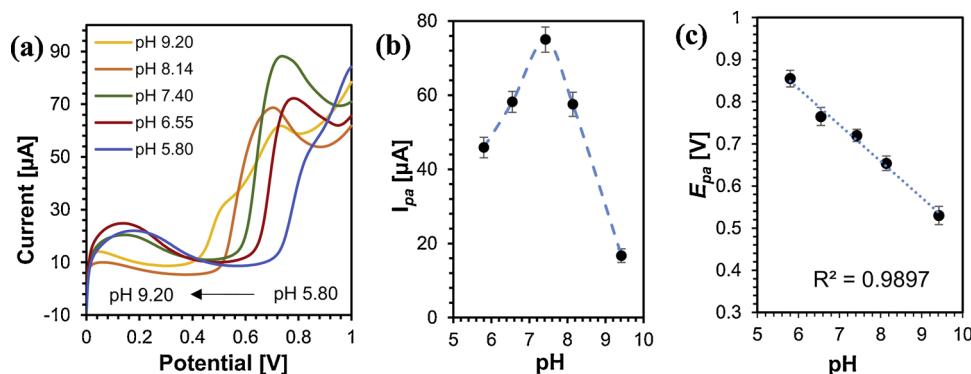
Fig. 6. (a) LSV of MWCNTs-βCD(Chem)/SPCE at different pH (5.80 to 9.20) in 0.01 M PBS with 30 μM BPA at scan rate 60 mVs^{-1} (b) The relationship between oxidation peak currents(I_{pa}) of BPA and pH of electrolyte (c) The dependency of oxidation peak potential (E_{pa}) on pH.

Faraday constant, $E°$ is the standard redox potential, and $K°$ is the standard rate constant of the reaction. From the linear regression of E_{pa} vs. $ln\nu$, the slope of the line as shown in Eq. (3), is $0.0479 = \left(\frac{RT}{\alpha n F}\right)$; which is used to evaluate the value of an to be 0.905. Usually, for a complete irreversible process, α = 0.5 is considered. Therefore, the number of electron transfer (n) is 2 for BPA oxidation at MWCNTs-βCD (Chem)/SPCE. The results in Fig. 5(a) show that higher scan rate results in increased oxidation current and voltage which may distort the oxidation peak, thus, in this work we took 60 mVs^{-1} as optimum value for the electrochemical sensing of BPA.

3.4. Effect of pH on BPA sensing

The pH of buffer solution has significant influence in acid-base dissociation of BPA, resulting in its changes of oxidation potential and current [56]. pH-dependent behavior of BPA sensing was investigated in the PBS buffer with 30 μM BPA using LSV. Fig. 6 represents the variation of peak oxidation current (I_{pa}) as well as peak oxidation potential (E_{pa}) with a standard deviation error bar as a function of the pH of the electrolyte. I_{pa} increased with pH until 7.4, then there was a sharp decrease as shown in Fig. 6(b), which indicates that protons involved in MWCNTs-βCD/SPCE and BPA reaction process [53]. MWCNTs − COOH and βCD are used as precursors to synthesis covalently modified MWCNTs-βCD using one-step steglich esterification [50]. At basic solution, with the increase of pH the residual carboxylic groups (− COOH) at the surface of MWCNTs are more deprotonated and exist as acidic anions that repulse the phenolic oxide anions of BPA, subsequently reduces the oxidation current. Thus, PBS of pH 7.4 was used for the sensing of BPA in this work.

The relationship between oxidation peak potential and the pH is presented in Fig. 6(c). The oxidation peak potential decreased with an increase in pH which can be expressed by the following linear regression equation:

$$E_{pa}(V) = -0.086pH + 1.3501 (R^2 = 0.9897) \tag{5}$$

According to Eq. (5), each unit of pH causes an 86 mV shift in oxidation peak potential which is slightly higher than the theoretical Nernst slope (59.5 mV pH^{-1}). Therefore, oxidation of BPA at MWCNTs-βCD/SPCE involves 2 electrons and 2 protons.

3.5. Voltammetric determination of BPA

Magnetic stirring of the sample improved the BPA oxidation current of the modified working electrode. The influence of magnetic stirring on the oxidation current is shown in Fig. SI 3. For the calibration curve of BPA detection, we used 20 min of magnetic stirring before each LSV scan. In voltammetric determination of BPA, two dynamic linear ranges of 0.125 - 2 μM and 2 - 30 μM were observed. Fig. 7(a) and (c) illustrates the LSV curves for the BPA concentration ranges of 0.125 - 2 μM

and 2 - 30 μM respectively, at a scan rate of 60 mVs^{-1}. From the figures, it is observed that oxidation occurs at the potential ranges of 0.72 V-0.75 V. In LSV scan, each curve has a baseline as well. The baseline subtracted results are presented in Fig. SI 4(a) and SI 4(b) for the Fig. 7(a) and (c) respectively. Fig. 7(b) and Fig. 7(d) represents the calibration curves for the concentration (C) ranges of 0.125 – 2 μM and 2 - 30 μM respectively, with standard deviation error bar.

The linear regression equations of Fig. 7(b) and (d) can be expressed as follows:

$$I_{pa}(\mu A) = 7.1944C(\mu M) - 0.5317(R^2 = 0.997) [0.125 - 2\,\mu M, \text{Fig. 7(b)}] \tag{6}$$

$$I_{pa}(\mu A) = 2.159C(\mu M) + 11.586(R^2 = 0.995)[2 - 30\,\mu M, \text{Fig. 7(d)}] \tag{7}$$

The slope of the two linear regions are different due to concentration dependent oxidation kinetics of BPA. While the oxidation kinetics of BPA at low concentration ($0.125 - 2$ μM) was associated with adsorption of BPA, the oxidation kinetics at high concentration was related to both adsorption and diffusion of BPA [57]. Thus, the slope at high concentration (2.159 μA/μM) is smaller than the slope at low concentration (7.1944 μA/μM). When the BPA concentration is higher than 30 μM, we observed that I_{pa} began to deviate from linear characteristics and became saturated. The limit of detection (LoD) was calculated using the following equation [58]:

$$LoD = 3s/m \tag{8}$$

Where s is the standard deviation of the blank solution (0.033 μA), and m is the slope of the calibration curve (7.1944 μA/μM). The LoD (SNR = 3) was 13.76 nM. The high sensitivity of MWCNTs-βCD synthesized by steglich esterification can be attributed to the moderate amount of βCD attachment at the end of MWCNTs [50]. Table 1 shows the comparison of our work with other carbon–based nanomaterials modified electrodes reported by different research groups for the detection of BPA. A good electrochemical sensor possesses several properties such as low LoD, wide linear range, and low cost. Table 1 shows that our sensor shows comparable LoD than that of other reports, but with a higher linear range. Moreover, we achieved these performances at a lower cost and with simpler fabrication processes. For example, the c-MWCNTs/ GCE sensor reported in [59] offered LoD of 5 nM with linear range (LR) of 0.01–10 μM while our proposed sensor provided LoD of 13.76 nM with LR of 0.125–30 μM (3 times higher LR than [59]). Wider LR is desirable for detecting a wide concentration range of target analyte. Also, we used a screen-printed carbon electrode (SPCE) which is much cheaper than that of a glassy carbon electrode (GCE).

Acronyms

C60/GCE = Fullerene/ glassy carbon electrode

CS/N-GS/GCE = Chitosan/nitrogen modified graphene sheet/ glassy carbon electrode
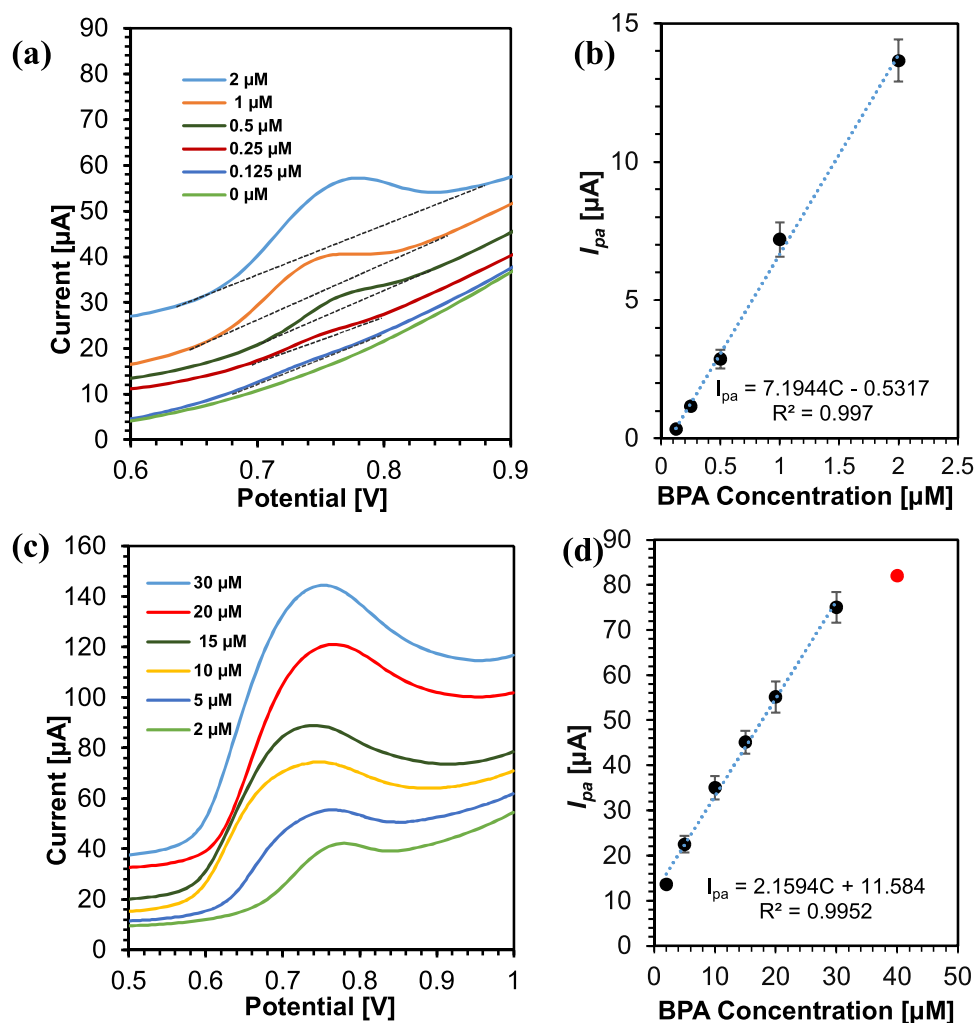
Fig. 7. (a) LSV of chemically modified MWCNTs-βCD/SPCE in 0.01 M PBS (pH 7.4) with the presence of 0.125 − 2 μM BPA at scan rate 60 mVs^{-1}, (b) The calibration curve (I_{pa} vs. concentration) of BPA from the graph (a), (c) LSV of chemically modified MWCNTs-βCD/SPCE in 0.01 M PBS (pH 7.4) with the presence of 2-30 μM BPA (d) the calibration curve (I_{pa} vs. concentration) of BPA from the graph (c).

Gr–CNTs/Pt = Graphene-carbon nanotubes/platinum

EG = Exfoliated graphene

PGA/MWCNT-NH$_2$= polyglutamate Acid/ amino-functionalized multiwall carbon nanotubes

c-MWCNTs/GCE = Carboxylated- multiwall carbon nanotubes/ glassy carbon electrode

CS/MNPs-rGO/GCE = Chitosan/ magnetic nanoparticles-reduced graphene oxide/ glassy carbon electrode

CS/MWCNT/GONRs/GCE = Chitosan/ multiwall carbon nanotubes/Graphene oxide nano-ribbons/ glassy carbon electrode

f-SWCNT/PC4/GCE = functionalized-single wall carbon nanotubes /carboxylic-functionalized poly/ glassy carbon electrode

Au/ssDNA/SWCNT = Gold/single strand DNA/ single wall carbon nanotubes

Table 1
Comparison of the carbon nanomaterial-based electrochemical sensors for BPA detection.

| Electrode	Detection method	Limit of detection, LoD (μM)	Linear Range (μM)	Reference
C60/GCE	SWV	0.0037	0.074 − 0.23	[33]
Li$_4$Ti$_5$O$_{12}$/MWCNTs/GCE	DPV	0.0780	0.1 − 10	[37]
Gr–CNTs/Pt	DPV	0.0420	0.06 − 10	[39]
PGA/MWCNT-NH$_2$	DPV	0.0200	0.1 − 10	[41]
c-MWCNTs/GCE	LSV	0.0050	0.01 − 10	[59]
f-SWCNT/PC4/GCE	CV	0.0320	0.099 − 5.794	[42]
MWCNT-GNPs/GCE	DPV	0.0075	0.02 − 20	[60]
Au/ssDNA/SWCNT	DPV	0.0110	0.5 − 3.8	[61]
CS/MNPs-rGO/GCE	DPV	0.0170	0.06 − 11	[38]
EG	SWV	0.7600	1.56 − 50	[62]
CS/N-GS/GCE	Amperometric	0.0050	0.01 − 1.3	[40]
CTAB/SPCE	SWV	0.0510	1.0 − 10	[63]
MWCNTs-βCD/SPCE	LSV	0.0137	0.125 − 2/ 2 − 30	This Work
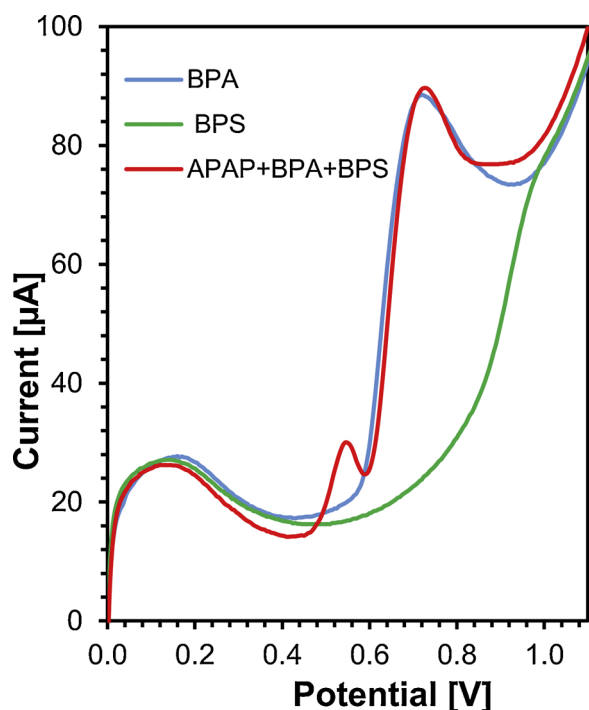
Fig. 8. LSV on MWCNTs-βCD/SPCE with 20 μM Bisphenol A (BPA), 20 μM acetaminophen (APAP), 20 μM Bisphenol S (BPS) in 0.01 M PBS (pH = 7.4) with 0.0027 M potassium chloride and 0.137 M sodium chloride at scan rate 60 mV/s.

I-t = current –time plot
CTAB/SPCE = cetyltrimethylammonium bromide/screen-printed carbon electrode
MWCNTs-βCD/SPCE = multiwall carbon nanotubes-β cyclodextrin/screen-printed carbon electrode

3.6. Interference

A highly selective BPA sensor is critical because there are many interference elements present in real water including pharmaceutical contaminants, salts, and plastic pollutants. Furthermore, previously, differently synthesized MWCNTs-BCD based electrochemical sensors have been used to detect acetaminophen (APAP) [64] and Bisphenol S (BPS) [65]. In this work, LSV was performed to investigate the selectivity of the MWCNTs-βCD(Chem)/SPCE electrode to BPA with interferences from APAP, BPS, and salt. From Fig. 8 it is observed that in the blend (APAP + BPA + BPS curve), APAP, BPA, and BPS were oxidized at MWCNTs-βCD(Chem)/SPCE electrode about at 0.55 V, 0.73 V, and 1.05 V respectively. The considerable amount of separation among the oxidation potential of those compounds as well as low oxidation peak current of APAP and BPS compared with BPA indicate that the modified working electrode is highly selective and sensitive towards BPA. It was examined that the presence of APAP and BPS did not affect the peak oxidation current and voltage of BPA, as compared with only BPA as shown in Fig. 8. In our previous study, cyclic voltammetry results (Fig. 4 (solid red line) in [64]) showed E_{pa} = 0.35 V and I_{pa} = 12 uA of 100 μM APAP using MWCNTs-βCD(Phys)/GCE electrode with scan rate of 20 mV/s at pH 7.4 [64]. In the present study, the higher oxidation potential (E_{pa} = 0.55 V) and higher oxidation current (I_{pa} =18 μA) of APAP are probably due to a high scan rate (60 mV/s).

3.7. Stability and reproducibility

To check the suitability of the electrode for practical use, the stability and reproducibility of the modified working electrode were

Table 2
Determination of BPA in real samples.

Sample	Added (μM)	Found (μM)[a]	Recovery
Lake water	1	1.087	108.70 %
	10	10.15	101.50%
	15	14.67	97.80%
	20	20.82	104.10%
	30	29.84	98.47%
Tap water	1	1.036	103.60%
	10	10.47	104.70%
	15	15.15	101.01%
	20	19.93	99.66%
	30	28.81	96.05 %

[a] Average values calculated from 3 determinations.

examined. After preparing the electrode we preserved it at room temperature for 35 days. Then we did 10 LSV measurements for 20 μM BPA. On average, the peak oxidation current retained its 91.2 % original response which attributed to very good stability of the MWCNTs-βCD/SPCE electrode. To do the reproducibility test, we prepared 10 MWCNTs-βCD/SPCE electrode and did 10 LSV measurements using those electrodes for 20 μM BPA. The relative standard deviation (RSD) of modified electrodes was 4.7 %, representing excellent reproducibility of the MWCNTs-βCD/SPCE electrode.

3.8. Determination of BPA in real samples

To check the suitability of the sensor for environmental (water) sensing, we did a recovery test of BPA within real samples such as lake water (from Bayfront, Hamilton, Canada) and tap water using LSV under optimal experimental conditions. We used the standard addition method for the recovery test. First, we prepared 1 mM BPA stock solution using methanol and then, we added an appropriate amount of 0.01 M PBS solution (pH 7.4) to prepare specific concentration of BPA (e.g. 1 μM, 10 μM, 15 μM, 20 μM, and 30 μM). Table 2 illustrates that the sensor demonstrated an excellent recovery from 96.05% to 108.7%.

4. Conclusions

We fabricated a very cheap, simple, and highly sensitive electrochemical sensor for the detection of BPA based on MWCNTs-βCD modified screen-printed carbon electrode. Due to the very high effective surface and excellent electrochemical behavior of MWCNTs as well as host-guest interaction capability of βCD, the sensor exhibited outstanding oxidation activity toward BPA sensing. The chemically mixed MWCNTs-βCD modified electrode performed better than the physically mixed MWCNTs-βCD modified electrode. The sensor offered a low limit of detection of 13.76 nM. Comparing with the BPA level in real water, the sensor provided a wide two–step linear response ranges from 0.125 to 2 μM and 2 to 30 μM. Finally, our sensor was successfully tested to determine the BPA level in lake and tap water, which show excellent recoveries of 97.8%–108.7%. The sensor provided excellent stability, reproducibility and high selectivity towards BPA detection even in the presence of interference species. Therefore, this sensor may be a good choice for low-cost rapid sensing of BPA in real water.

Credit author statement

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.
Notes
The authors declare no credit author statement

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2020.128319.

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Md Younus Ali is a PhD student in Department of Electrical and Computer Engineering at McMaster University, Hamilton, Canada. He received a B. Sc. Eng. degree in Electronic and Communication Engineering from Khulna University in 2008 and received a M.A.Sc. degree in Nanotechnologies for ICTs, Politecnico di Torino, Italy in 2016. His research focuses on design and development of low cost 2D materials-based electrochemical sensors for environmental and health monitoring.

Arif Ul Alam is currently a post-doctoral fellow in Department of Electrical and Computer Engineering at McMaster University, Hamilton, Canada. He received a B.S. degree in Electrical and Electronic Engineering from Islamic University of Technology, in Dhaka, Bangladesh in 2008 and received a M.A.Sc. degree in Electrical and Computer Engineering at McMaster University, Hamilton, ON, Canada in 2013, and a PhD degree in Electrical and Computer Engineering at McMaster University, Hamilton, ON, Canada in 2019. His research focuses on design and development of low cost electrochemical sensors for environmental and health applications.

Matiar M. R. Howlader received a B. Sc. Eng. degree in Electrical and Electronic Engineering from Khulna University of Engineering and Technology, in Khulna, Bangladesh, in 1988, and his M.S. and Ph.D. degrees in Nuclear Engineering from Kyushu University, Fukuoka, Japan, in 1996 and 1999, respectively. Currently, Dr. Howlader is an Assistant Professor in the Department of Electrical and Computer Engineering at McMaster University, Hamilton, ON, Canada. His research focuses, broadly, on the design, fabrication, characterization, and development of new materials and novel engineered components to create integrated sensing systems for health, environmental and energy heavesting applications. For this, in particular, he develops foundational technologies in the surface activated nanobonding currently, emphasizing on the flexible, soft and hard materials integration for the sensing systems that enable energy harvesting.