

Electrochemical Determination of Bisphenol A on Multi-Walled Carbon Nanotube/ titanium dioxide Modified Carbon Paste Electrode

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Abstract— we present a novel electrochemical sensor for highly sensitive and selective determination of Bisphenol A (BPA) using differential pulse voltammetry (DPV). It is based on multi-walled carbon nanotubes-titanium dioxide modified carbon paste electrode (MWCNT/TiO₂PE). For characterization of the CNT/TiO₂PE, cyclic voltammetry (CV) was employed. The modified electrode exhibited lower overpotentials in comparison to bare carbon paste electrode (CPE). The fabricated electrochemical sensor displayed a linear and sensitive response to BPA within the concentration range of 1×10^{-6} to 6×10^{-4} M. The detection limit was found to be 3×10^{-6} M.

Index Terms— Bisphenol A; Electrochemical sensor; Carbon paste electrode, Multi-walled carbon nanotube, Differential pulse voltammetry.

1 INTRODUCTION

BPA is an organic synthetic monomer which has potential demands in chemical industries. It is a recyclable and durable polymer that is broadly employed for packing drinking water bottles, containers, lens of glasses, baby bottles and reusable food containers industries[1, 2]. Since it is extensively used in various areas of human life, nowadays, a major concern has arisen about it[3, 4]. Because BPA is distributed in our environment from different kinds of the poly-carbonate products and epoxy resin coatings. It has been popularized as an endocrine disrupter. Widespread studies confirm that BPA has extensive adverse side effects to human health and wild-life [5-8]. It can mimic hormones, estrogens and androgens in the endocrine system[9]. Furthermore, it can badly affect central nervous system (CNS)[10]. Also, BPA has been proven to cause declining sperm counts and birth defect due to its hormone-like behavior[11]. In addition, BPA can lead to various kind of cancers such as prostate and breast cancer, diabetes, heart diseases and obesity[12, 13]

Because of aforesaid serious hazards of BPA to the environment and human health, a reliable monitoring system for measuring the levels of BPA has become an urgent issue. Up to now, the current methods mainly used for detection of BPA were of the instrument-based methods comprise gas chromatography- mass spectrometry (GC-MS) [14-17], liquid chromatography- mass spectrometry[18], liquid chromatography with electrochemical detection (LC-ED)[19], enzyme-linked immunosorbent assay (ELIA) [20, 21], fluorescence detection[22] and high-performance liquid chromatography[23, 24]. In spite of high sensitivity and remarkable selectivity of these methods, they are not normally used for detection of BPA, owing to the complexity and high cost of their equipment, their need to expert operators and the need of much time to prepare samples[25-27]. By comparison, electrochemical sensors attract more attentions owing to their reliability, fast response speed, low cost, simplicity, time-saving, cheap instruments and high sensitivity.

As shown in Figure 1, BPA has two hydroxyphenyl groups. Thus, it's an electrochemically active compound [28-30]. On the other hand, it has displayed poor response at traditional electrochemical sensors because of fouling effects of bare electrodes. In order to solve this problem materials with electrocatalytic activity, high stability and excellent conductivity should be applied. In this regard, MWCNT due to its small size and good electrochemical properties is of enormous inter-

est[31].

TiO₂ as a metal oxide has attractive properties contain low cost, environmentally benign nature, non-toxicity, conductivity and high specific surface area[32]

Herein, a new electrochemical sensor based on CNT/TiO₂ modified carbon paste electrode was constructed to improve determination of BPA. It was found that the oxidation peak current of BPA remarkably increased at the surface of CNT/TiO₂PE versus to bare CPE. The performance of fabricated sensor was evaluated using CV and DPV techniques and results indicating that CNT and TiO₂ are suitable sensing materials to measure the levels of BPA.

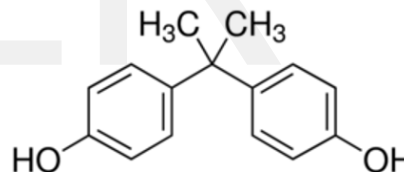


Fig. 1 Chemical structure of BPA

2 MATERIALS AND METHODS

2.1 Chemical and Materials

BPA was purchased from Sigma Aldrich, K₂HPO₄ and KH₂PO₄ for preparation of phosphate buffer solution, graphite powder, paraffin oil, potassium chloride and K₄Fe(CN)₆ were obtained from Merck. CNT and TiO₂ were purchased from Merck. All other reagent were of analytical grade and used as received without further purification. The phosphate buffer solution was prepared of 0.1 M K₂HPO₄ and 0.1 M KH₂PO₄ stock solutions at pH 7. The stock solution of 1×10^{-2} M BPA was made by dissolving the chemical in to methanol (HPLC grade) and then stored at 4 °C in the dark. All other solutions were prepared with deionized water.

2.2 Apparatus

A potentiostat/ galvanostat (IVIUM TECHNOLOGY – VERTEX) was applied to perform the electrochemical techniques. A conventional three-electrode system was employed

for all electrochemical measurements: a CNT/TiO₂ modified carbon paste working electrode, a platinum wire auxiliary electrode and an Ag | AgCl electrode as reference electrode.

2.3 Preparation of CPE and CNT/TiO₂PE

The unmodified carbon paste electrode was prepared by hand-mixing of graphite and paraffin oil at a ratio of 70:30 (w/w) and mixed well to form a homogeneous paste. Then, a portion of the prepared paste was packed in to the end of the glass tube. The electric contact was made via forcing a copper wire in to the other end of the glass tube connected to the mixture. Before preparation of carbon paste electrode, glass tube was perfectly smoothed. Also, the prepared electrode was polished using a piece of weighing paper and then washed with deionized water before each use. CNT/TiO₂PE was prepared in the same way and by the addition of appropriate amount of CNT and TiO₂ to the graphite in the first step.

3 RESULTS AND DISCUSSION

3.1 Electrochemical Characterization of BPA

According to previous studies[33] for determination of BPA, neutral pH (pH 7) was found as the optimum amount. Therefore, the peak current is the maximum amount at this pH.

Figure 2 displays the cyclic voltammograms of 1×10⁻⁴ M BPA at various modified electrodes. As shown in Figure 2, the oxidation peak current of BPA increased for the following electrodes, respectively: CPE, CNTPE, TiO₂PE and CNT/TiO₂PE, indicating that the modification of CPE using CNT-TiO₂ exhibited significant enhancement effects due to the high conductivity of CNT and excellent surface area of TiO₂. According to the curves, all of the electrodes displayed an irreversible oxidation peak within the potential range of 0 to 1V demonstrating the irreversible electrochemistry of BPA. The bare CPE, TiO₂PE, CNTPE and CNT/TiO₂PE display the oxidation peak current of around 14.6, 35.8, 38.2 and 45.2 μA for BPA, respectively.

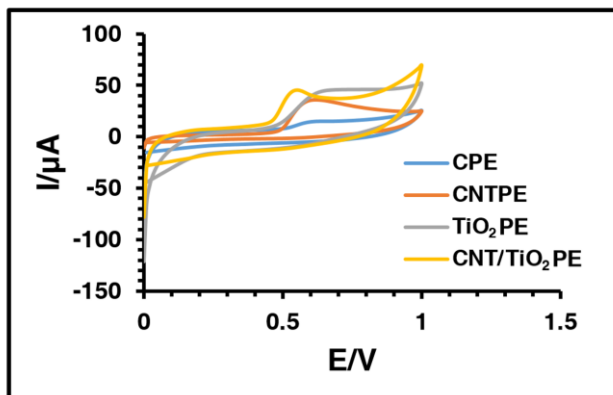


Fig. 2 Cyclic voltammograms of 1×10⁻⁴ M at various modified electrodes.

3.2 Electrochemical Characterization of CNT/TiO₂PE

Cyclic voltammetry was performed for investigation of the structure and electrochemical properties of CNT/TiO₂PE (Figure 3). It was carried out in 5mM Fe(CN)₆^{3-/4-} solution containing 0.1 M KCl as redox probe.

Figure 3 shows the CVs at bare and modified electrodes. The oxidation peak current was increased clearly from 41.841 μA at bare electrode to 54.315μA at CNT/TiO₂PE. Moreover peak to peak separation (ΔE_p) enhanced lightly from 0.05 for bare CPE to 0.1 for CNT/TiO₂PE. The results indicate that CNT and TiO₂ can improve the conductivity and sensitivity of the carbon paste electrode.

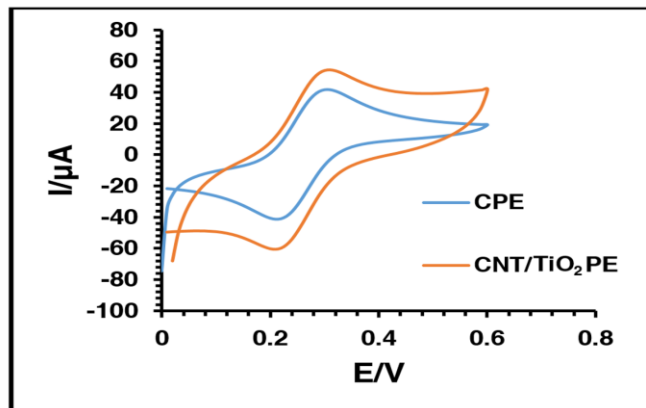


Fig. 3 Cyclic voltammograms of bare CPE and CNT/TiO₂PE in 5mM Fe(CN)₆^{3-/4-} (1:1) solution containing 0.1M KCl. Scan rate: 50mVS⁻¹.

3.3 Effect of Scan Rate

As shown in Figure 4A, cyclic voltammetry was employed to evaluate the effect of scan rate on electrochemical oxidation of BPA in 1×10⁻⁴ M BPA solution. As can be seen in Figure 4A, with the increasing scan rate, the oxidation peak current of BPA was enhanced gradually, indicating a linear relationship between the scan rate and peak current of BPA (Figure 4B). It can be attributed to the adsorption-controlled process of the oxidation of BPA at CNT/TiO₂PE. Also, there is a relationship between E_p and logarithm of V (log v) according to equation 1 (Figure 4C). The electron transfer coefficient (α) was calculated to be 0.6 from equation 2:

$$E_p = 0.5308 + 0.0392 \log v \quad (1)$$

$$b = 2.303RT/n(1 - \alpha)F \quad (2)$$

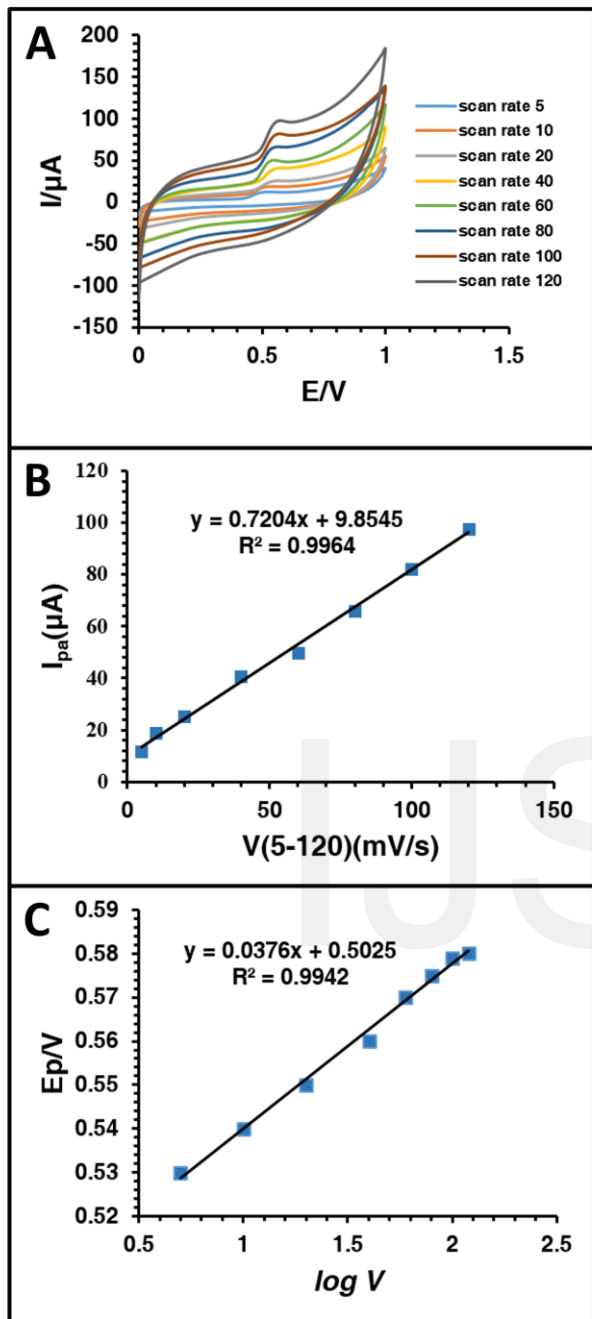


Fig. 4 (A) Cyclic voltammograms of 1×10^{-4} M at CNT/TiO₂PE with different scan rates (B) The plot for the dependence of peak current on the scan rate (C) the relationship between E_p and $\log V$.

Where α is transfer coefficient, n is number of electron transferred, R is the gas constant, T is the absolute temperature, and F is the faraday constant.

3.4 Determination of Detection Limit

DPV was carried out to determine the lowest limit of detection of BPA at the surface of CNT/TiO₂PE. As can be seen in Figure 5A, in the concentration range of 1×10^{-6} to 6×10^{-4} M, the

oxidation peak current of BPA increased significantly with enhancement of the concentration of BPA. Thus, a linear relationship between the peak current of BPA and its concentration was attained (Figure 5B) according to the equation 3:

$$i_p = 0.0209 \mu A L mol^{-1} x [BPA] + 69.905 \quad (3)$$

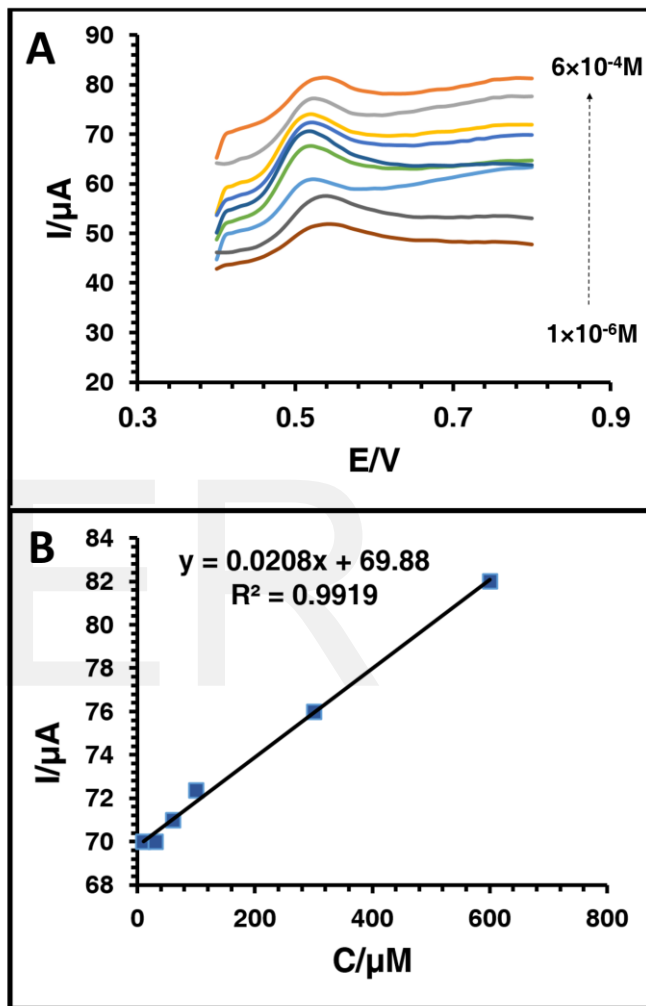


Fig. 5 (A) voltammograms of BPA at various concentrations (B) Calibration curve of BPA.

The detection limit of BPA using this method was attained as low as (3×10^{-6} M).

4 CONCLUSION

This work develops a convenient but sensitive, rapid and reliable electrochemical sensor based on CNT/TiO₂PE for determination of BPA. Compared to bare electrode, at the CNT/TiO₂PE the oxidation peak current of BPA was remarkably increased. Also, a negative shift can be observed in the

peak potential of BPA. Results can be related to the conductivity and catalytic activity of CNT/TiO₂. Having high sensitivity, low detection limit, simplicity and wide linear range of this sensor are the reasons that encourage us to employ it for determination of BPA in real samples.

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