Anal. Bioanal. Electrochem., Vol. 10, No. 9, 2018, 1108-1119

Analytical & Bioanalytical Electrochemistry

www.abechem.com

Full Paper

MnO_2 Nanorods Modified Screen Printed Electrode as a Novel Voltammetric Sensor for Specific Detection of Bisphenol A

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Received: 28 November 2017 / Received in revised form: 5 December 2017 / Accepted: 26 December 2017 / Published online: 30 September 2018

Abstract- Bisphenol A (BPA) is an effective endocrine-disrupting compound (EDC) that causes adverse effects on human health and environment. This study reported a novel bisphenol A sensor via MnO_2 nanorods modified screen printed electrode. The prepared MnO_2/SPE presented fast response, high sensitivity and low background current. Differential pulse voltammetry (DPV) was used as an analytical method for the quantitative determination of bisphenol A, and the fabricated electrochemical sensor exhibits a linear response to bisphenol A in the range of 1.0–300.0 μM with the limit of detection (LOD) of 0.5 μM at a signal-to-noise ratio of 3. The prepared MnO_2/SPE has been successfully used for detecting bisphenol A in water samples.

Keywords- Bisphenol A, MnO_2 nanorods, Voltammetric Sensor, Screen Printed Electrode, Real Samples

1. INTRODUCTION

Bisphenol A (BPA) is known as one of the important endocrine disruptors which is commonly used in an intermediate step in the production of epoxy resins and polycarbonate

plastics. Thus, polycarbonate plastics, especially the food and beverage containers (water and milk bottles, baby bottles), fire retardants and dental filling materials may contain bisphenol A [1]. By virtue of its very wide field of use, humans may routinely be exposed to bisphenol A in their daily lives. Bisphenol A, owing to its structure similar with estrogen hormone, imitates the hormonal activity and functions as an endocrine disruptor by binding estrogen receptors which results in many adverse effects on biological systems of both humans and animals. Numerous studies showed that bisphenol A displays induced enlargement in the number of fat cells and caused weight gain in both people and laboratory mice. In addition to this effect, it is known that bisphenol A can lead to problems such as decrease in fertility, resistance to insulin, cardiovascular disorders, diabetes, cancer and thyroid disorder [2]. Consequently, to protect health, the use of bisphenol A in baby bottles have been banned in many countries and its content of residue in food packages is limited to 3 mg/kg [3]. Thus, highly selective and sensitive analysis of bisphenol A remains its significance due to the various potential sources for bisphenol A contamination. Up to now, a number of approaches have been brought forward in literatures, such as the enzyme linked immune sorbent assay, liquid chromatography–mass spectrometry, gas chromatography–mass spectrometry, fluorescence, surface-enhanced Raman scattering and high-performance liquid chromatography [4-9]. However, most of the mentioned detection approaches need complicated pretreatment due to its higher requirements for the extraction and purification of the sample. In addition, some shortcomings such as exorbitant implement, time-consuming and unsuitability for onsite detection further limit its application [10-21]. By comparison, electrochemical sensors access to a great research enthusiasm due to their portability, credibility, onsite inspection, fast response and low cost.

Screen-printed electrodes (SPEs), are disposable sensors that depend on screen-printing technology, they are made by printing various types of inks on different ceramic or plastic substrates. Moreover, the SPEs surface could be easily altered to fit many purposes interrelated to various analytes and to attain a diversity of enhancements. Also, electrodes could be modified by depositing several substances on the electrodes surfaces [22-24].

However, the response signal of conventional sensors towards analytes detection are quite weak, which makes it very difficult to achieve accurate measurements of analytes [25-39]. Therefore, in order to improve the response signal of the analyte determination, electrochemical sensors modified with advanced materials such as molecularly imprinted polymer, quantum dots, metal nanoparticles based composites and carbon based materials have been ceaselessly fabricated for the detection of analytes [40-52].

Particularly, the electrode materials based on metal oxides have received intensive attention due to their high capacitance and fast redox kinetics. Manganese dioxide (MnO_2) has been demonstrated to be one of promising modifier on account of its fascinating theoretical capacitance, abundant resource, low cost as well as environmentally benign nature

[53,54]. Remarkably, the nanostructures of MnO_2 (at least one dimension < 100 nm, e.g. nanoparticles, nanoflakes, nanowires, nanorods etc.), have exhibited greatly enhanced capacitive performances than those of bulk counterpart, because of their high specific surface area and optimized material utilization [55]. Compare with other nanostructures, the one dimensional (1-D) nanostructures usually exhibit additional advantages due to their unique structure and surface properties [56].

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a general purpose electrochemical system software. The surface morphology of the composites was analyzed with KYKY, EM 3200 Scanning Electron Microscopy (SEM).

The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, a silver pseudo-reference electrode and an unmodified graphite working electrode. pH was measured by a Metrohm 710 pH meter.

Bisphenol A and all other reagents were analytical grade, and were purchased from Merck (Darmstadt, Germany). For the preparation of buffers, the orthophosphoric acid and its salts were used to provide the pH range of 2.0–9.0.

2.2. Synthesis of MnO_2 nanorods

2.5 mmol $KMnO_4$ and 1 mL concentrated HCl were mixed with 45 mL deionized water and stirred for 30 min to form a precursor solution, which was then transferred into a 250 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and hydrothermally treated at 140 °C for 12 h.

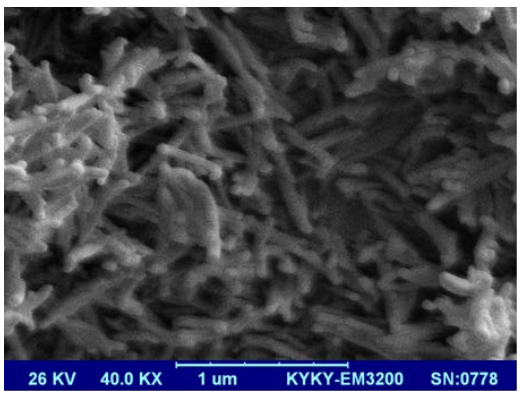

Fig. 1. SEM image of MnO_4 nanorods

After the autoclave was cooled naturally to room temperature, samples depositing at the bottom were collected and washed by centrifugation for several cycles using deionized water and absolute ethanol. The as-synthesized samples were then dried in 60 °C. A typical SEM image of synthesized MnO_2 nanorods is shown in Fig. 1.

2.3. Preparation of the modified electrode

The bare screen-printed electrode was coated with MnO_2 nanorods according to the following simple procedure. 1 mg MnO_2 nanorods were dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5 µl of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until becomes dry.

3. RESULT AND DISCUSSION

3.1. Electrochemical profile of the bisphenol A on the MnO_2/SPE

To study the electrochemical behaviour of bisphenol A which is pH-dependent, it is necessary to obtain the optimized pH value in order to achieve the accurate results. By performing the experiments by use of modified electrodes at various pH values ranging from 2.0–9.0, it was revealed that the best results for electro-oxidation of bisphenol A occur at pH=7.

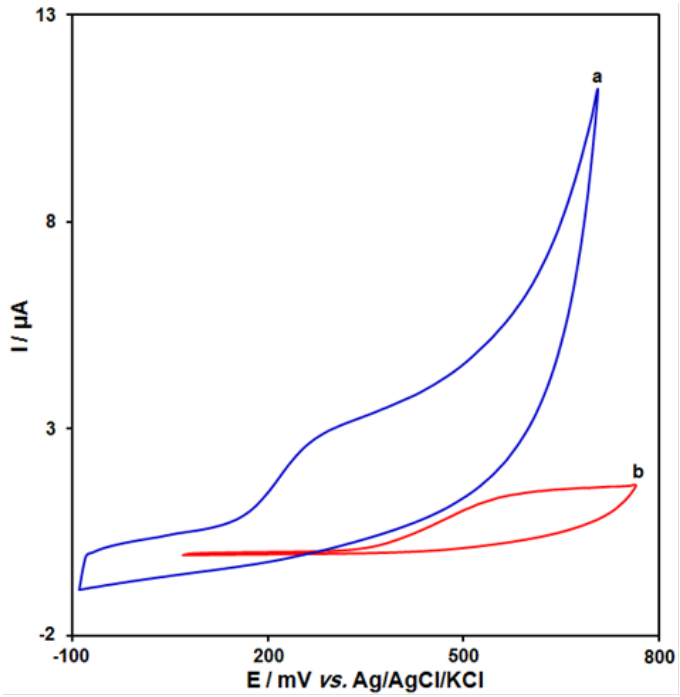

Fig. 2. Cyclic voltammograms of (a) MnO_2/SPE and (b) unmodified SPE in 0.1 M PBS (pH 7.0) in the presence of 300.0 µM bisphenol A at the scan rate 50 mVs^{-1}

The obtained cyclic voltammograms in the presence of 300.0 µM bisphenol A using the MnO_2/SPE (carve a) and unmodified SPE (carve b) are shown in Fig. 2. According to CV results the maximum oxidation of bisphenol A on the MnO_2/SPE occurs at 300 mV which is about 280 mV more negative compared with unmodified SPE.

3.2. Effect of scan rate on the results

Increasing in scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of bisphenol A, Fig. 3. In addition, there is a linear relationship between Ip and the square root of the potential scan rate ($\nu^{1/2}$) that demonstrates that the oxidation procedure of analyst is in control of diffusion.

The Tafel curve of analyte was plotted applying the data from the rising sections (i.e. the Tafel regions) of the current–voltage curve obtained at 10 mVs^{-1} (Fig. 4). The kinetics of electron transfer in the electrode reaction, influence on the Tafel regions of the current potential curve. The Tafel slope was obtained 0.1794 V implying to an electron rate determining step (RDS) in the electrode process with charge transfer coefficient (α) of 0.67 [57].

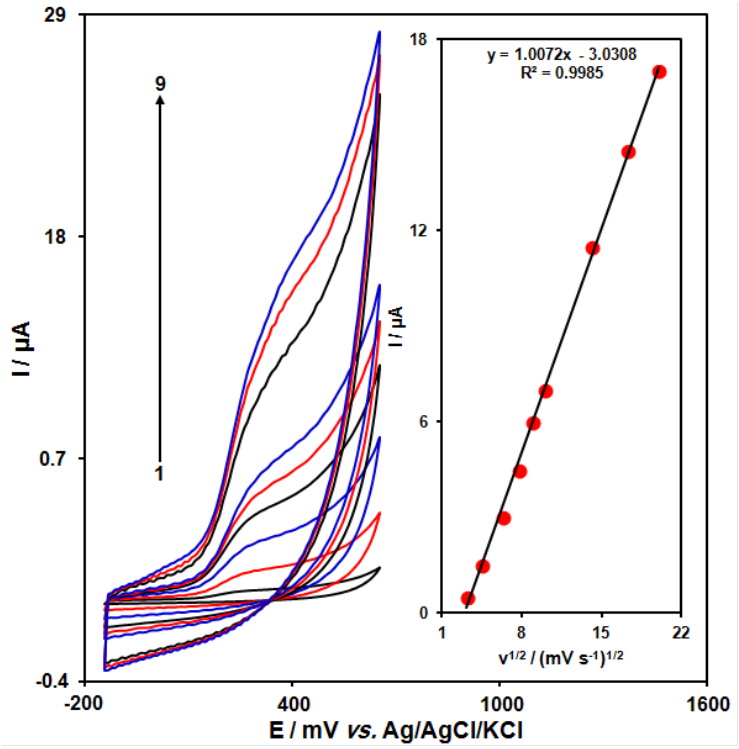

Fig. 3. CVs of MnO_2/SPE in 0.1 M PBS (pH 7.0) containing 300.0 µM bisphenol A at various scan rates; numbers 1-9 correspond to 10, 20, 40, 60, 80, 100, 200, 300 and 400 mV s^{-1}. Inset: Variation of anodic peak current *vs.* $\nu^{1/2}$

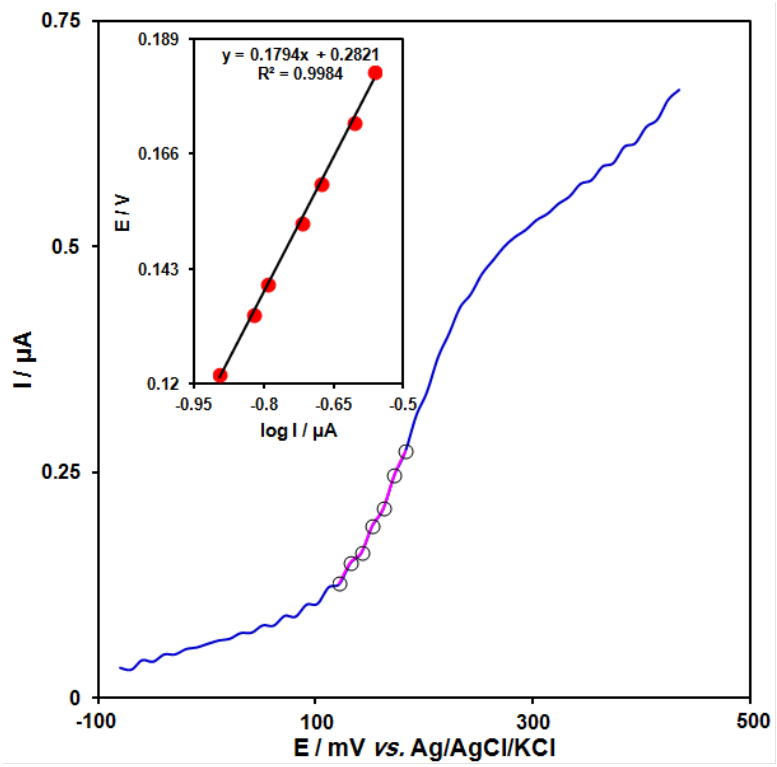

Fig. 4. LSV (at 10 mV s^{-1}) of electrode in 0.1 M PBS (pH 7.0) containing 20.0 µM vitamin B6. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the LSV

3.3. Chronoamperometric analysis

The analysis of chronoamperometry for bisphenol A samples was performed by use of MnO_2/SPE *vs.* Ag/AgCl/KCl (3.0 M) at 0.4 V. The Chronoamperometric results of different concentration of bisphenol A sample in PBS (pH 7.0) are demonstrated in Fig. 5. The Cottrell equation for chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as follow [57]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Where D represents the diffusion coefficient (cm^2 s^{-1}), and C_b is the applied bulk concentration (mol cm^{-3}). Experimental results of I *vs.* $t^{-1/2}$ were plotted in Fig. 5A, with the best fits for different concentrations of bisphenol A. The resulted slopes corresponding to straight lines in Fig. 5A, were then plotted against the concentration of bisphenol A (Fig. 5B). The mean value of D was determined to be 1.8×10^{-5} cm^2/s according to the resulting slope and Cottrell equation.

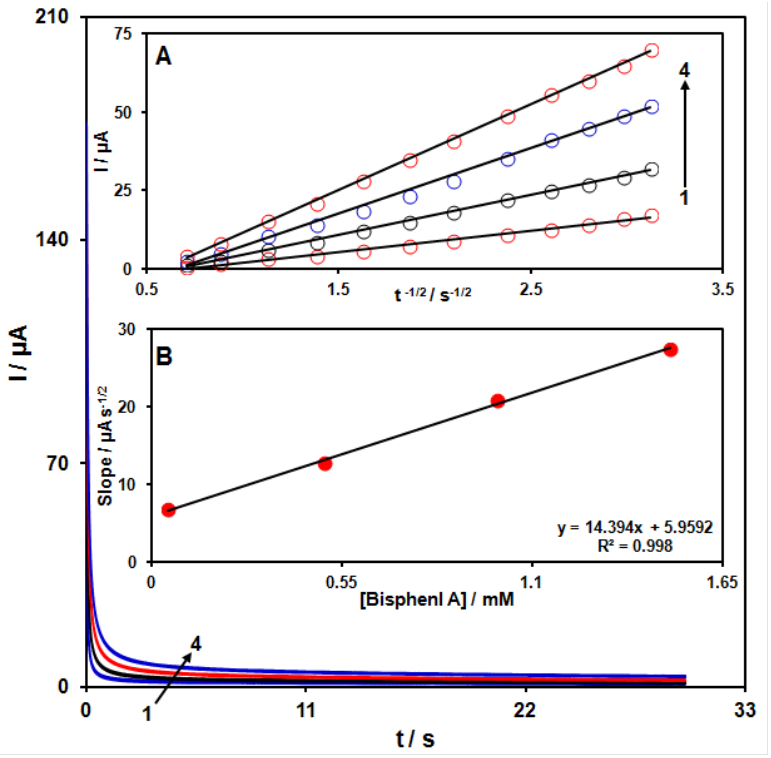

Fig. 5. Chronoamperograms obtained at MnO_2/SPE in 0.1 M PBS (pH 7.0) for different concentrations of bisphenol A. The numbers 1–4 correspond to 0.05, 0.5, 1.0 and 1.5 mM. (A) Plots of I *vs.* $t^{-1/2}$ obtained from chronoamperograms 1-4. (B) Plot of the slope of the straight lines against bisphenol A concentration

3.4. Calibration curve

Based on the resulting peak currents of bisphenol A by use of MnO_2/SPE, the quantitative analysis of bisphenol A was done in water solutions. The modified electrode (MnO_2/SPE) as working electrode in the range of bisphenol A concentration in 0.1 M PBS was used in differential pulse voltammetry (DPV) due to the advantages of DPV including the improved sensitivity and better performance in analytical applications (Fig. 6) (Initial potential=0.09 V, End potential=0.37 V, Step potential=0.002 V, Modulation Amplitude=0.02505 V). According to the results, a linear relationship exists between the peak currents and concentrations of bisphenol A within the concentration range of 1.0-300.0 µM with the correlation coefficient of 0.999. The detection limit was obtained 0.5 µM. Table 1. shows a comparison of the analytical figures of merit of the proposed electrochemical method with different reported modifier for the determination of bisphenol A.

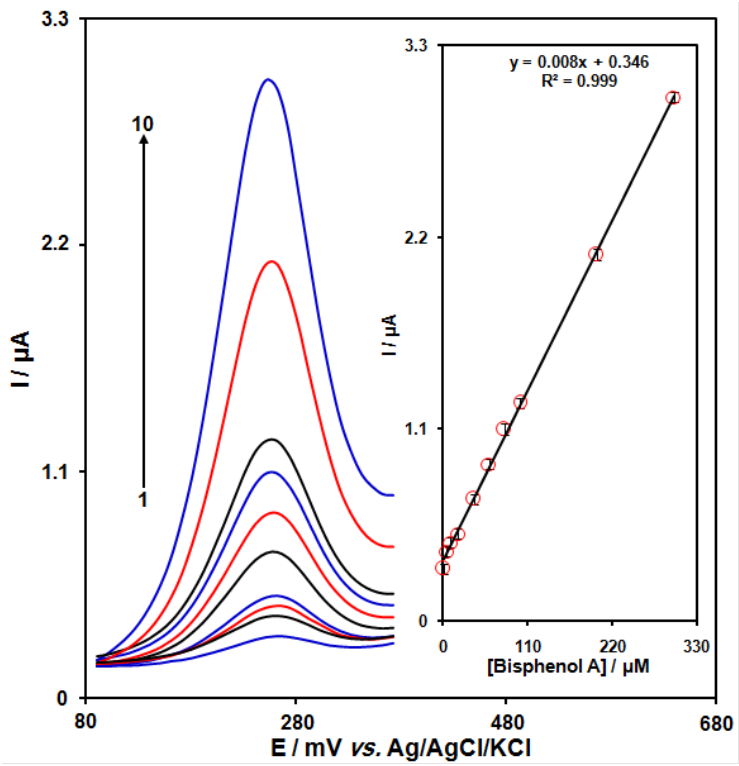

Fig. 6. DPVs of MnO_2/SPE in 0.1 M PBS (pH 7.0) containing different concentrations of bisphenol A. Numbers 1–10 correspond to 1.0, 5.0, 10.0, 20.0, 40.0, 60.0, 80.0, 100.0, 200.0 and 300.0 µM. Inset: Plot of I *vs.* bisphenol A concentrations. In all cases the scan rate was 50 mV s^{-1}

Table 1. Comparison of the efficiency of some methods used in detection of bisphenol A

Method	Modifier	LOD	LDR	Ref.
Voltammetry	Multiwalled carbon nanotube and gold nanoparticle	4.0 nM	0.01-0.7 µM	[58]
Voltammetry	Reduced graphene oxide-silver/poly-L-lysine nanocomposites	0.54 µM	1.0-80.0 µM	[59]
Voltammetry	graphene oxide and cuprous oxide nanocomposite	0.053 µM	0.1-80.0 µM	[60]
Voltammetry	Reduced graphene oxide-multi-walled carbon nanotubes	0.001 µM	0.005-20.0 µM	[61]
Voltammetry	AuPd nanoparticles-loaded graphene nanosheets	8.0 nM	0.5-10.0 µM	[62]
Voltammetry	MnO_2 nanorods	0.5 µM	0.1-300.0 µM	This work

3.5. Analysis of real samples

The applicability of this modified electrode in the determination of real samples was assessed through the determination of bisphenol A in water sample using the described method. In order to perform this analysis, standard addition method was employed and the results are listed in Table 2. Accordingly, the results of bisphenol A recovery is satisfactory and the reproducibility of the results is proved by the mean relative standard deviation (R.S.D.).

Table 2. The application of MnO_2/SPE for determination of bisphenol A in water samples (n=5). All concentrations are in μM

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Well water	0	-	-	-
	5.0	5.1	102.0	2.9
	10.0	10.2	102.0	1.6
	15.0	14.8	98.7	1.8
	20.0	19.8	99.0	3.5
River water	0	-	-	-
	7.5	7.4	98.7	2.8
	12.5	12.3	98.4	3.7
	17.5	17.7	101.1	2.4
	22.5	22.6	100.4	1.5

4. CONCLUSION

The present study focused on a fabrication of a graphite sensor with MnO_2 nanorods for the efficient detection of bisphenol A in different matrixes. Thanks to the excellent electro-catalytic property and high adsorption capacity of MnO_2 nanorods, the oxidation peak current of bisphenol A was enhanced significantly compared with the unmodified electrode. The electrochemical performance of the modified sensor was carried out by DPV with a linear range of 1.0-300.0 μM and a low detection limit as 0.5 μM. Also the developed sensor system was applied in real samples with a high accuracy. These results demonstrated that the MnO_2 nanorods will be a promising modification material for the electrochemical detection of various analytes.

Acknowledgments

The authors acknowledge the financial support provided for this project (No. 96/914) by the Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology, Kerman, Iran.

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