Facile and Sensitive Determination of bisphenol A Based on MWCNTs-TiN Nanocomposites Modified Glassy Carbon Electrode

Jing-Yi Wang[1], Jin-Wei Zhang[1], Huan-Huan Xu[2], Wei-Xin Lv[2], Fen-Ying Kong[2,], Wei Wang[2,*]*

[1] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, China
[2] School of Chemistry and Chemical Engineering, Yancheng Institute of Technology, Yancheng 224051, China
[*]E-mail: kongfy@ycit.edu.cn, wangw@ycit.edu.cn

Herein, a novel and convenient electrochemical sensor based on a glassy carbon electrode modified with multi-walled carbon nanotubes-titanium nitride (MWCNTs-TiN) film for sensitive and efficient detection of bisphenol A (BPA) was developed. Several important parameters controlling the performance of the sensor, such as scan rate, the volume of MWCNTs-TiN dispersion and the pH value of buffer solution, were be investigated and optimized by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). It was notable that the oxidation peak current of BPA had enhanced greatly and the oxidation overpotential had decreased significantly. Under the optimized conditions, the oxidation peak current was proportional to BPA concentration in the range of 0.1-50μM, and the detection limit was 0.05μM. Meanwhile, the modified electrode was also exhibited good reproducibility and stability, and was employed to *in-situ* determinate BPA in water samples with satisfying results.

1. INTRODUCTION

Bisphenol A (BPA), namely 2,2-bis (4-hydroxyphenyl) propane, is a chemical intermediate widely used in the synthesis of daily plastic products, such as epoxy resin, polycarbonate and polystyrene resins [1]. Also, BPA is an endocrine disruptor, which can mimic the body's own hormones and may lead to adverse impact on wildlife and human beings [2]. A large number of studies have pointed out that people exposure to high level BPA are more likely to result heart disease,

coronary heart disease, diabetes, liver damage, even various cancers [3]. BPA not only has harmful effects on human health, but also on environment. Many evidences have indicated that BPA can migrate into environment via various paths, such as the manufacturing process of plastics, the degradation process of waste plastics [4]. So, it is very important and necessary to develop a simple, sensitive, rapid and reliable analytical method to detect and monitor of BPA for public health and environmental security.

Up to now, various methods for BPA determination have been built, such as high performance liquid chromatography, gas chromatography, capillary electrophoresis, fluorescence, chemiluminescence, enzyme linked immunosorbent assays and electrochemical sensors [5-11]. Among them, electrochemical sensors are the ideally analytical tools owing to its high sensitivity, short analysis time, good handling convenience, low analytical cost and real-time detection in situ condition [12]. However, at bare electrode, BPA shows the very poor response signals due to the fouling effects. In addition, BPA oxidation also involves a relatively higher overpotential, which lowers the selectivity and sensitivity [13]. To solve this problem, novel electrode modified material with high stability, good catalytic activity and excellent conductivity must be developed.

Carbon nanotubes (CNTs), molecular-scale wires, are attractive nanomaterials because of their excellent conductivity, strong adsorptive ability, and large specific surface area [14]. Specially, multi-walled carbon nanotubes (MWCNTs) can be considered as a fast electron-transport network because of the coexistence of ballistic and diffusive transport and the tubular morphology [15]. Electrode modified with MWCNTs has been widely developed for electrochemical sensing. On the other hand, titanium nitrides (TiN) recently have also attracted much attention owing to its desirable properties, such as noble-metal-like properties, superior conductivity, low cost, outstanding catalytic properties, as well as excellent biocompatibility [16,17]. TiN has been widely used in energy conversion, Li-air batteries, supercapacitors, electrochemical sensor and so on.

The purpose of the present work is to explore a novel electrochemical sensor for simple and sensitive determination of BPA. To address this, TiN nanoparticles were anchored on the MWCNTs network, and the obtained nanocomposites were used to modify the surface of glassy carbon electrode (GCE). It was found that the obtained nanocomposites modified electrodes (MWCNTs-TiN/GCE) showed good performance for electrochemical sensing of BPA. The effects of the determination conditions were optimized in details. Finally, the proposed sensor was applied to determine BPA in water samples and the obtained results were satisfying.

2. EXPERIMENTAL

2.1. Reagents

MWCNTs were purchased from Chengdu Organic Chemicals Co. Ltd. Before use, MWCNTs were treated by mixed acid in order to purify and segment MWCNTs for easier and better dispersion [15]. Tetrabutyl titanate was obtained from Aladdin Reagent Co. Ltd. BPA was bought from Sigma Co. (USA). BPA was dissolved into ethanol to prepare 0.1 M standard solution, and stored at 4 °C.

Working solutions were freshly prepared before use by diluting the standard solution. All other reagents were of analytical grade and without further purification. Ultrapure water from a Milli-Q Plus system (Millipore) was used throughout the experiment. 0.1 M Phosphate buffer solutions (PBS) with various pH values were prepared by mixing stock standard solutions of Na_2HPO_4 and NaH_2PO_4, then using H_3PO_4 and NaOH to adjust the pH value.

2.2. Apparatus

The morphology and microstructure of the samples were characterized with transmission electron microscopy (TEM, JEM-2100F) and scanning electron microscopy (SEM, S-4800). The electrochemical measurements were performed on a CHI 660D electrochemical workstation. A conventional three-electrode system was employed, including a bare or the MWCNTs-TiN/GCE (diameter, 3 mm) serving as the working electrode, Ag/AgCl electrode and platinum wire serving as the reference and counter electrodes respectively.

2.3. Preparation of MWCNTs-TiN nanocomposites

TiN nanoparticles were prepared according to our previously reported method [16]. Then, as obtained TiN nanoparticles (10 mg) were dissolved in 10 mL different concentration of MWCNTs suspension. The concentration of MWCNTs suspension was 1, 5, 10, 20 mg mL^{-1}, respectively. Finally, with the aid of ultrasonication, a uniform dispersion was obtained.

2.4. Fabrication of modified electrode

For the fabrication of MWCNTs-TiN nanocomposites modified GCE, the bare GCE was firstly polished with 1.0, 0.3 and 0.05mm alumina slurries until a mirror like surface was obtained. Then, GCE was sonicated successively in distilled water and ethanol for 5 min, respectively. After dried under nitrogen, 5 μL of as-prepared MWCNTs-TiN nanocomposites was coated on the surface. Finally, the as-obtained modified electrode was dried in air. This electrode was denoted as MWCNTs-TiN/GCE. For comparion, MWCNTs/GCE and TiN/GCE were also prepared in a similar method. When not in use, the modified electrode was stored at 4 °C in a refrigerator.

2.5. Analytical procedure

For the electrochemical determination of BPA, different concentrations of BPA were added into the electrochemical cell which contained 10 mL of PBS (0.1 M, pH 6.0). After the three-electrode system was immersed in the cell, the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were recorded. The oxidation peak current was measured for quantitative analysis of BPA. All experiments were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. Material characterization

*3.1. Structure and morphology characterization*

Structure and morphology of the prepared samples were investigated using TEM. Fig. 1 showed typical TEM micrographs of TiN (A), MWCNTs (B) and MWCNTs-TiN nanocomposites (C). As displayed in Fig.1A, the TiN nanoparticles exhibited an ideal cubic structure with a size of approximately 50 nm. From Fig. 1B, it could be found that a highly bundled and entangled tubular structure appeared with 20-40 nm in diameter, which was consistent with earlier report [18]. After hybridization of TiN particles with MWCNTs, many cubes were clearly found on the surface and sidewall of nanotube, demonstrating that TiN successfully combined with MWCNTs. The introduction of TiN nanoparticles to the MWCNTs played an important role which can overcome the van der Waals interaction between the MWCNTs and thus prevent MWCNTs from agglomeration. The morphology of the MWCNTs-TiN nanocomposites was also investigated by SEM. As shown in Fig. 1D, the MWCNTs bundles were interconnected together to form a netlike nanostructure. Some white spots, which were TiN nanoparticles, were randomly dotted on the netlike nanostructure. Such morphological structure is helpful to improve diffusion of the electroactive species and provide rapid response for the modified electrode.
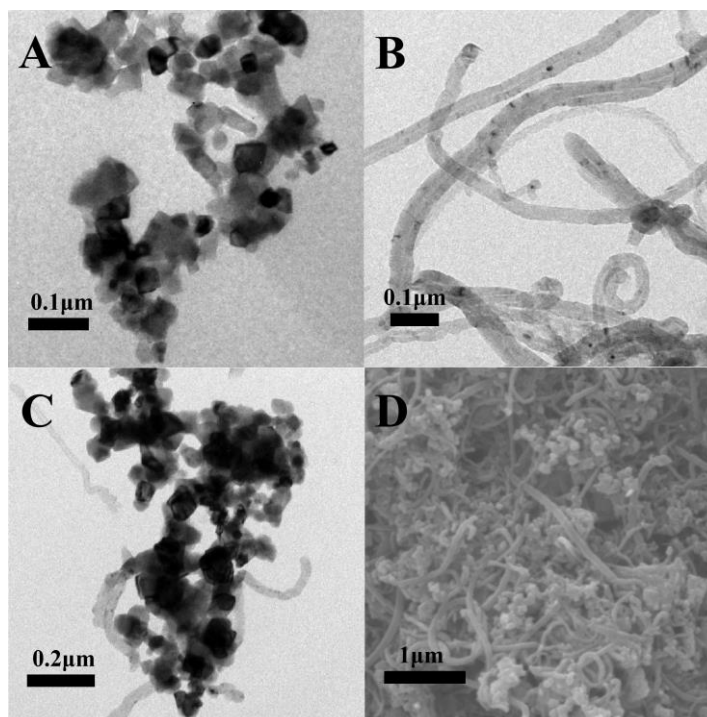
Figure 1. TEM images of TiN (A), MWCNTs (B), MWCNTs-TiN(C) and SEM image of MWCNTs-TiN(D).

3.2. Electrochemical behaviors of BPA

Fig. 2 showed the cyclic voltammograms of 10μM BPA at different modified electrodes. As illustrated, an oxidation peak was observed in the potential scanning from 0.0 V to 1.2 V at each modified electrode. However, no corresponding reduction peak of BPA was presented in the reverse scan, which indicated that the oxidation reaction was totally irreversible. On the other hand, at the TiN modified electrode, a relatively small oxidation peak was observed (curve a). After the GCE coated with MWCNTs individual, a higher current response appeared (curve b), suggesting that MWCNTs act as an effective electron promoter for electrocatalytic oxidation of BPA. Interestingly, a remarkable enhancement in oxidation peak current accompanying a low oxidation potential was obtained at the MWCNTs-TiN/GCE (curve c), indicating the synergistic effect between MWCNTs and TiN.
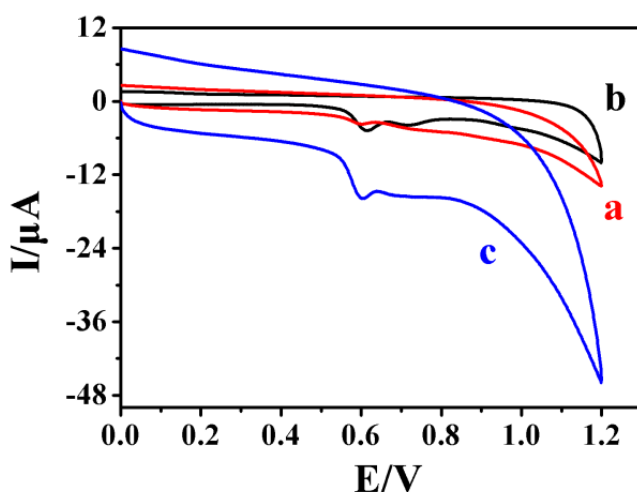
Figure 2. Typical CVs of 10μM BPA at a MWCNTs/GCE (a); TiN/GCE (b) and MWCNTs-TiN/GCE (c) in 0.1 M PBS (pH 6.0). Scan rate: 100mVs[-1].

3.3. Optimization of experimental conditions

3.3.1. Effect of pH values

The pH of the solution considerably influences the electrochemical behavior of BPA. The effect of pH value was investigated in the pH range from 3.0 to 8.0 and the results were shown in Fig.3A. As illustrated, the oxidation peak current of BPA increased obviously with the increase of pH value from 3.0 to 6.0, and then decreased quickly with further improving of pH value, showing that protons had taken part in the electrode reaction processes [19]. Therefore, pH 6.0 PBS was selected as the optimized value for the subsequent analysis. Furthermore, from Fig.3A, it also can be found that the oxidation peak potential shifted negatively along with the increase of pH value and a good linear relationship was observed between the E_{pa} and pH values. The linear regression equation was: $E_p/V = -0.0614$ pH$+1.017$ (R=0.970). According to the Nernst equation, the slope of 61.4mV/pH indicated that equal numbers of electrons and protons are involved in the electrooxidation of BPA [20].
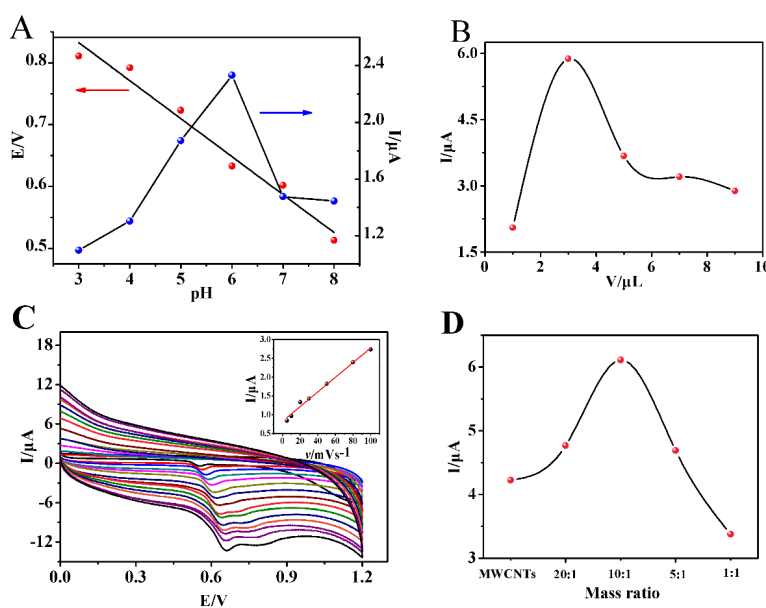
3.3.2. Effect of the volume of MWCNTs-TiN dispersion

The volume of MWCNTs-TiN dispersion coated onto the electrode surface had a predominant influence on the voltammetric response of BPA. Fig.3B demonstrated the influence of the volume of MWCNTs-TiN dispersion on the oxidation peak current of 10 μM BPA. As can be observed, the oxidation peak current of BPA increased remarkably with varying the volume of MWCNTs-TiN dispersion from 0 to 3 μL. Further increasing the volume of MWCNTs-TiN dispersion, the peak current conversely decreased. This was probably due to the limited mass transport of BPA inside a thicker film, resulting in a decline of the peak current [21]. So, 3 μL of MWCNTs-TiN dispersion was employed to fabricate the modified electrode.

3.3.3. Effect of scan rate

The influence of scan rate on the electrochemical behavior of BPA at MWCNTs-TiN/GCE was recorded and the results were shown in Fig. 3C. As can be seen, the oxidation peak current of BPA increased gradually with the increase of scan rate. A good liner relationship between the oxidation peak current (I_p) and the scan rates (v) was obtained in the range from 5 to 100 mV s^{-1} (inset of Fig. 3C). The regression equation was $I_p/\mu A = 0.8273 + 0.0195 \, v$, r = 0.990. This result suggested that the reaction was adsorption-controlled process. In this work, the scan rate was chosen as 100 mV s^{-1}.

*3.3.4. Effect of the fraction of TiN in the nanocomposites*

Figure 3. (A) Effects of solution pH value on the oxidation peak current and oxidation peak potential of BPA at MWCNTs-TiN/GCE; (B) Effects of the volume of MWCNTs-TiN dispersion on the oxidation peak current of BPA; (C) CVs of BPA at MWCNTs-TiN/GCE with different scan rates. Inset: plots of oxidation peak current of BPA versus scan rates; (D) Effects of the fraction of TiN in the nanocomposites on the oxidation peak current of BPA.

The amount of TiN played an important role in the determination of BPA. As well known, the intrinsic van der Waals interactions between the pristine tubes make MWCNTs bundles in scale and insoluble in routine solvents [22]. The introduction of TiN can act as "spacers" to prevent MWCNTs agglomeration. So, the MWCNTs-TiN nanocomposites exhibited good dispersion in water. As shown in Fig. 3D, the oxidation peak currents of BPA increased with increasing TiN content in the nanocomposites. It reached a maximum value at the mass ratio of 10:1 (MWCNTs/TiN) and decreased with further increasing TiN content, which is probably attributed to the smaller conductivity of TiN. So, the mass ratio was fixed at 10:1 for further investigation in this work.

3.4. Analytical curve

Under the optimized experimental conditions, the analytical performance of the MWCNTs-TiN/GCE toward BPA was evaluated by using the more sensitive DPV as the detection method. Fig. 4A displays the DPV curves for various concentrations of BPA in 0.1 M PBS (pH 6.0) at the MWCNTs-TiN/GCE. As can be seen, the oxidation peak current increased with increasing concentration of BPA. The oxidation peak current was linearly related to BPA concentration in the range from 0.1 to 50µM, as illustrated in Fig. 4B. The linearity regression equation was $i_p/\mu A = 0.06844 - 0.08621c$ ($R^2 = 0.9982$), and the detection limit was estimated to be 0.05µM (S/N = 3). Table 1 lists the various parameters for BPA detection in comparison with those of reported sensors using other nanomaterials. From Table 1, it is obvious that the MWCNTs-TiN/GCE exhibited the comparable or even better analytical performance. The reason might be attributed to the synergistic effect of MWCNTs and TiN in the nanocomposites. Hence, MWCNTs-TiN was an excellent electrode modification material for BPA detection.
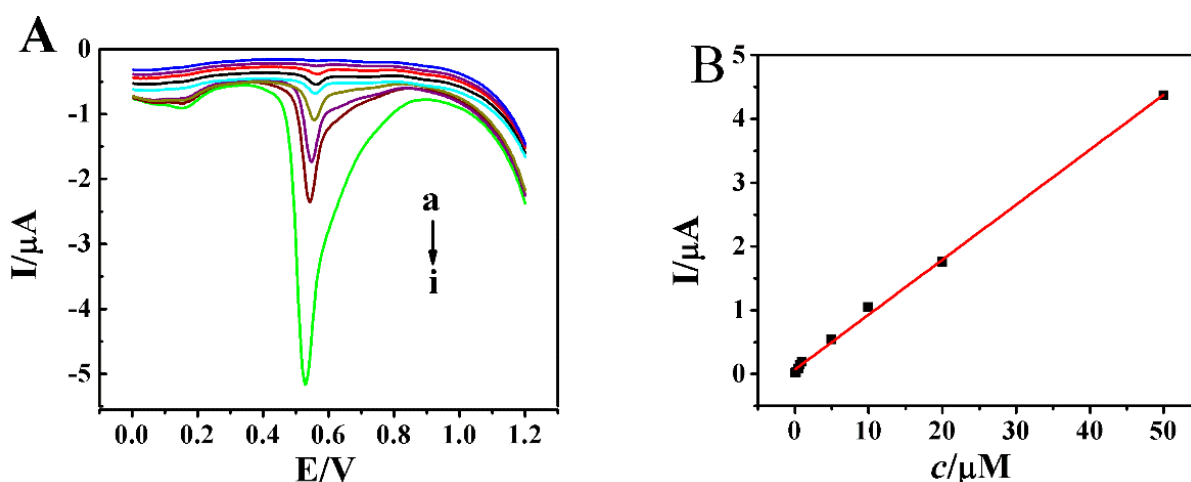
Figure 4. (A) DPV curves for various concentrations BPA at MWCNTs-TiN/GCE in 0.1 M PBS (pH 6.0) (a-i, 0.1-50µM). (B) The relationship between the oxidation peak current and the concentration of BPA.

Table 1. Summary of sensing characteristics of the MWCNTs-TiN/GCE for BPA detection along with those reported in literature

Working electrodes	Linear range (µM)	LOD (µM)	Ref.
PGA/MWCNT-NH$_2$/GCE	0.1-10	0.02	[23]
MCM-41/CPE	0.22-8.8	0.038	[24]
SPCE/PEDOT/BMIMBr	0.1-500	0.02	[25]
CMK-3/nano-CILPE	0.2-150	0.05	[26]
PEDOT/GC	90-410	55	[27]
NCNF/CPE	0.1-60	0.05	[28]
MWCNTs-TiN/GCE	0.1-50	0.05	This wok

3.5. Selectivity, reproducibility and stability

In order to evaluate the selectivity of the proposed electrochemical sensor, the influence of some possible interfering substances such as common phenolic complexes, inorganic ions were tested under optimal conditions. It was found 50-fold concentration of *p*-nitrophenol, *o*-nitrophenol, phenol, pyrocatechol, 2,4-dinitrophenol, and hydroquinone had no obvious influence on the oxidation peak current of BPA (peak current change<5 %). In addition, some inorganic ions such as 100-fold concentration of Na^+, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{3+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^- did not interfere the determination of BPA with the deviation below 5%. These results revealed that the proposed electrochemical sensor has high selectivity for BPA detection.

Reproducibility and stability were sequentially performed to examine the modified electrode performance. The relative standard deviation (RSD) for the oxidation peak currents of 10 µM BPA was 4.74% for different electrodes fabricated by the same procedure. This result indicated that the modified electrode had excellent reproducibility. The stability of the modified electrode was investigated by keeping the modified electrode at 4 °C in a refrigerator when not in use. After two weeks, the peak current of 10 µM BPA retained 90.5% of its initial response. This phenomenon demonstrated that the modified electrode also had good stability.

3.6. Analysis of water samples

To evaluate the practical application of proposed method, the modified electrode was employed to *in situ* detect BPA in water samples. Three sections of water samples collected from the river of yanchen institute of technology were simply filtrated to remove the undissolved substance. There was no need for the further sample pretreatment. After that, 1 mL of sample solution was spiked into an electrochemical cell containing 9 mL of 0.1 M PBS (pH 6.0). BPA was detected with the fabricated MWCNTs-TiN/GCE using standard addition method and analyzed by DPV. The measurement results were shown in Table 2. Clearly, the amount of BPA was about 0.81µM, 0.79µM and 0.75µM in west, middle and east water samples. In addition, the recoveries were achieved in the range from 97.0 % to

107 %, revealing that the present procedure was feasible and valid for the determination of BPA in practical samples.

Table 2. Determination results of BPA in water samples

Samples	Measured value	Added	Founded	Recovery
West water	0.81μM	0.50μM	1.40μM	107%
Middle water	0.79μM	0.50μM	1.25μM	97.0%
East water	0.75μM	0.50μM	1.32μM	106%

4. CONCLUSION

To sum up, a simple and sensitive electrochemical sensor for the determination of BPA was successfully developed by modifying the GCE surface with MWCNTs-TiN nanocomposites. Due to synergic effects of MWCNTs and TiN, the modified electrode displayed excellent performance to BPA with wide linear range and low detection limit. The proposed method was applied in the determination of BPA in water samples with satisfactory results. Moreover, the proposed electrochemical sensor showed good stability, selectivity and reproducibility. This strategy might open more opportunities for *in-situ* determination of BPA with simple preparation and low cost.

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