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Novel Electrochemical Sensor Based on MnO₂ Nanowire Modified Carbon Paper Electrode for Sensitive Determination of Tetrabromobisphenol A

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Abstract: In this paper, a MnO₂ nanowire (MnO₂-NW) modified carbon paper electrode (CP) was developed as a novel electrochemical sensor for the sensitive determination of tetrabromobisphenol A (TBBPA). The MnO₂ nanowire was prepared by a hydrothermal synthesis method, and the morphology and structure of MnO₂ were characterized using scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The electrochemical performance of TBBPA on MnO₂-NW/CP was investigated by cyclic voltammetry, and the result confirmed that MnO₂-NW/CP exhibited excellent sensitivity for the determination of TBBPA due to the high specific surface area and good electrical conductivity of the nanowire-like MnO₂. Moreover, the important electrochemical factors such as pH value, incubation time and modified material proportion were systematically studied to improve the determination sensitivity. The interferences from similar structure compounds on TBBPA have also been investigated. Under the optimal conditions, MnO₂-NW/CP displayed a linear range of 70~500 nM for TBBPA with a detection limit of 3.1 nM. This was superior to some electrochemical methods in reference. The work presents a novel and simple method for the determination of TBBPA.

Keywords: tetrabromobisphenol A; MnO2; carbon paper; modified electrode

1. Introduction

Tetrabromobisphenol A (TBBPA), an organic compound with the chemical formula $C_{15}H_{12}Br_4O_2$, is widely used as a reactive flame retardant in electronic equipment, furniture, plastics and textile products [1,2]. TBBPA accounts for 80% of the global demand in Asia. As a result of its massive use, release from industrial products, as well as the migration of terrestrial and marine food chains, TBBPA is continuously released into the environment [3–5]. TBBPA is a potential persistent organic pollutant reported to be bioaccumulative and highly toxic. Chronic exposure to TBBPA can induce immune, reproductive and neurotoxic effects on animals [6–8]. In 2017, the World Health Organization's International Agency for Research on Cancer published a preliminary list of carcinogens for reference, and tetrabromobisphenol A is on the list of carcinogens in category 2A. Therefore, detecting TBBPA quickly and accurately is important for environmental monitoring and the protection of human health.

Several analytical methods have been reported for the detection of TBBPA, including chromatographic [9,10], spectroscopic [11,12] and immunoassay methods [13,14]. For example, Zhang et al. [10] developed a high-performance liquid chromatography method coupled with triple quadrupole mass spectrometry (HPLC-MS/MS) with atmospheric pressure chemical ionization (APCI) source for simultaneous detection of TBBPA and its ten derivatives in determining complicated environmental samples, including sewage sludge, river water and vegetable samples. Feng et al. [12] explored a fluorescent sensor by coating a molecularly imprinted polymer layer on CdTe quantum dots for the sensitive determination



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of TBBPA. Although these methods have good selectivity and high detection sensitivity, they are limited by the high costs of instrument maintenance, sophisticated operating skills, and extensive organic solvent consumption. Many researchers pay attention to electrochemical sensors due to their high efficiency, low cost, prominent sensitivity, and rapid detection speed [15–17]. Presently, some electrochemical sensors have been reported for the detection of TBBPA in the environment. Nonetheless, some TBBPA electrochemical sensors' utility is limited by the non-conductive film that forms on the electrode surface due to TBBPA's electrochemical oxidation, impairing detection stability [18].

The materials used for electrode modification play a pivotal role in mitigating the passivation induced by TBBPA oxidation products. The conception and advancement of nanomaterials have considerably influenced electrochemical sensors, with their properties largely being a function of their microstructure and form. A variety of nanomaterials, such as metal oxides, carbon-based materials, metal-organic frameworks, and nanocomposites, are being studied for TBBPA detection. Zhou et al. [19] prepared a conductive composite of carbon nanotubes@zeolitic imidazole framework-67 (CNTs@ZIF-67), which possesses an excellent adsorption capacity (92.12 mg g^{-1}) for TBBPA. The composite was used to modify an acetylene black electrode for the sensitive determination of TBBPA in spiked rain and pool water samples with the aid of perfluorodecanoic acid. The sensor is stable, reproducible, and has a linear range of $0.01-1.5 \mu M$ TBBPA concentration, with a 4.2 nM detection limit (at S/N = 3). Recently, carbon dots (CDs) have attracted a lot of attention due to their low toxicity, biocompatibility and good electrical conductivity, and are widely used in biosensors, photocatalysis, electrocatalysis and electrochemical sensors. Guo et al. [20] developed magnetic CDs composed of carbon dots (CDs) and Fe₃O₄ nanoparticles via an amination reaction. A glassy carbon electrode modified with magnetic CDs and cetyltrimethylammonium bromide (CTAB) was employed as an electrochemical sensor for TBBPA detection in beverages. Magnetic CDs facilitate TBBPA oxidation, and CTAB's hydrophobic effect can enrich TBBPA. The combined impact of Magnetic CDs and CTAB boosts electrochemical sensor performance, indicating a linear range between 1 and 1000 nM, a detection limit of 0.75 nM, and displaying benefits such as rapidity, superior sensitivity, and robust stability. MXene, an exceptional electrode modification material, is a two-dimensional transition metal carbide obtained by etching aluminum in Ti_3AlC_2 with hydrofluoric acid. The combination of precious metals nanoparticles and Mxene can take advantage of the extraordinary electrocatalytic properties of noble metal nanomaterials and the specific surface area and electrical conductivity of MXene. Shao et al. [21] developed a TBBPA electrochemical sensor by modifying it to a glassy carbon electrode with the MXene/Au nanocomposite. The finalized sensor exhibited excellent linearity for TBBPA concentrations between 0.05 and 10 nM. It had a detection limit of 0.0144 nM and successfully detected TBBPA in water, with recoveries ranging from 97.1% to 106% for the added standards. Lu et al. [22] reported that the composite of graphitic carbon nitride $(g-C_3N_4)$ and N-butylpyridinium hexafluorophosphate (NBH) could promote the oxidation of TBBPA. The detection of TBBPA was fulfilled using a g-C₃N₄-NBH modified carbon paste electrode in the range of 1 nM to 30 nM and 30 nM to 500 nM with a limit of 0.4 nM.

Various metal oxides, including CuO, Fe₃O₄ and Fe₂O₃, have extensive applications in electrochemical sensors due to their distinct morphology [23–25]. Zhou and colleagues [23] produced different forms of CuO nanomaterials, namely nanostrips, nanowires, and microspheres. These were combined with graphene nanoplates and used to modify the surface of glassy carbon electrodes for electrochemical detection of both glucose and TBBPA. The composite made from CuO nanostrips demonstrated the most significant active surface area, the least charge transfer resistance, and the highest detection sensitivity. The designed electrochemical sensor offered sensitive TBBPA detection within a linear range of 5 to 600 nM, with an anticipated detection limit of 0.73 nM based on a signal-to-noise ratio of three. Luo et al. [24] developed an Fe₃O₄-activated biochar using surplus sludge, leading to the successful creation of an electrochemical sensor for TBBPA detection. The results from electrochemical tests suggested that the Fe₃O₄-activated biochar film possessed a

more substantial active surface area, reduced charge transfer resistance, and increased TBBPA accumulation efficiency. The sensor exhibited solid linearity for TBBPA concentrations ranging from 5 to 1000 nM, a reasonably low detection limit of 3.2 nM, and was effectively utilized to determine TBBPA in water samples. Zhang et al. [25] synthesized different morphologies of Fe₂O₃ nanomaterials such as nanoplate, nanorod and flower-like by a hydrothermal method. The electrochemical activity of Fe₂O₃ nanomaterial modified electrodes was found to be closely related to Fe₂O₃'s morphology. The composite of flower-like Fe₂O₃ (f-Fe₂O₃) and expanded graphite (EG) exhibited the largest electrochemical active area and the lowest electron transfer resistance. The f-Fe₂O₃/EG modified electrode displayed the best sensing performance of TBBPA with a detection limit of 1.23 nM.

Nano manganese dioxide (MnO₂) was widely used as electrode material owing to its extraordinary electrochemical performance, low cost, abundant storage, non-toxic nature and simplicity in preparation. Currently, MnO₂ nanomaterials show promising potential in solar cell devices, bioapplications, sensing, dye mineralization etc., because MnO_2 can be easily tuned into desired structure and morphology [26]. Different morphological MnO₂ nanoparticles prepared under specific conditions display varying electrochemical characteristics, boasting qualities such as excellent electrical conductivity, stability, and sensitivity [27–29]. Karami-Kolmoti et al. [28] exhibited a sensitive electrochemical sensor based on a manganese dioxide nanorods/graphene oxide nanocomposite for the determination of hydroquinone in water samples. Yu et al. [29] prepared novel manganese dioxide-graphene nanosheets (MnO_2 -GNSs) by a one-step hydrothermal method. A MnO₂-GNSs modified glassy carbon electrode was employed for the sensitive detection of hydrogen peroxide. Yakubu et al. [30] introduced a novel competitive electrochemical immunosensor built on gold-palladium bimetallic nanoparticles for quick and sensitive detection of TBBPA in environmental water. The nanoparticles were successfully synthesized and modified with amine-functionalized nanoflower-like manganese oxide. Under the best conditions, the competitive sensors demonstrated superb performance, including commendable sensitivity (LOD, 0.10 ng/mL; S/N = 3) and satisfactory accuracy (recovery rate, 84–120%). This proposed method has been applied in the analysis of TBBPA from various water sources, demonstrating the significant potential for the sensitive detection of trace amounts of TBBPA in aquatic settings. However, a non-enzymatic electrochemical sensor for the detection of TBBPA based on a MnO₂ nanowire modified electrode has not been reported.

In this work, an easy-to-use and sensitive electrochemical sensor, a MnO_2 nanowire modified carbon paper electrode, was fabricated for the sensitive detection of TBBPA. Carbon paper (CP) is a kind of rigid material composed of a complex and tortuous fibrous structure with a resin [31]. It is well known that the electrochemical behavior of sensors depends on their surface properties. Compared with other conventional electrodes, carbon paper electrodes possess some unique characteristics, such as adjustable size, porosity, conductivity and mechanical strength [32,33]. In addition, the use of carbon paper electrodes eliminates the tedious electrode grinding of solid electrodes, making miniaturization and portability possible and advancing on-line and in-situ measurements for electrochemical testing. The effects of pH, the usage of MnO_2 -NW/CP for the detection of TBBPA.

2. Materials and Methods

2.1. Chemicals and Instruments

The carbon paper (CP) used in this research was purchased from Toray (Japan). TBBPA and Potassium ferricyanide (K_3 [Fe(CN)₆]) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Potassium permanganate, sodium dihydrogen phosphate (NaH₂PO₄), dibasic sodium phosphate (Na₂HPO₄), N, N-Dimethylformamide (DMF), anhydrous ethanol and acetonitrile were purchased from Jiangsu Qiangsheng Functional Chemistry Co. Ltd. (Nanjing, China). All the chemicals were of analytical grade and used without further purification. All of the aqueous solutions were prepared with twice-

distilled water throughout the whole experiment. The experimental temperatures were all at room temperature.

All electrochemical experiments, including differential pulse voltammetry (DPV) and cyclic voltammetry (CV), were carried out in an electrochemical workstation RST 3000 with a three-electrode system. CP or modified electrode was used as the working electrode, and Ag/AgCl and Pt wire were used as the reference and auxiliary electrodes, respectively.

2.2. Fabrication of Manganese Dioxide

Manganese dioxide was prepared by two methods.

Method 1: 0.728 g of potassium permanganate was added to a mixture solution of 80 mL H₂O and 15 mL ethanol and then stirred at 25 °C for 2 h. After the reaction was completed, the product was washed 3 times with deionized water and anhydrous ethanol and dried in an oven at 60 °C for 12 h [34].

Method 2: 0.45 g of potassium permanganate was dissolved in 30 mL of 0.4 M acetic acid solution, transferred to a 50 mL Teflon-lined stainless-steel autoclave (Anhui Kemi Instruments Co., Hefei, China) and kept at 140 °C for 12 h. After the reaction was completed, the product was washed 3 times with deionized water and anhydrous ethanol and dried in an oven at 60 °C for 12 h.

2.3. Preparation of Modified Electrodes

The CP was cut into 1×0.5 cm and ultrasonically cleaned in ethanol for five minutes. The geometric area of the carbon paper electrode in solution was controlled to be 0.5×0.5 cm² with the insulating adhesive, and the upper end of the carbon paper electrode was connected to the electrochemical workstation. To excite the electrochemical properties of the CP [35], the electrode was immersed in 0.1 M sulfuric acid solution and scanned for 50 cycles from -0.2 V to 1.0 V at 100 mV/s using the CV method. Then, the electrode was cleaned with deionized water and dried at room temperature.

A total of 4.0 mg of manganese dioxide was dispersed in 2.0 mL of DMF solution with the aid of an ultrasonic bath to obtain a suspension of 2 mg/mL of manganese dioxide. Next, 7.0 μ L of the above suspension was dropped onto the surface of the treated carbon paper electrode and dried at room temperature.

3. Results and Discussion

3.1. Characterization of Manganese Dioxide

Scanning electron microscope (SEM) images were used to investigate the microstructures and morphologies of MnO₂ nanomaterials. Different microstructures and morphologies of MnO₂ nanomaterials were found when MnO₂ was prepared by different methods. As shown in Figure 1a, an irregular sheet structure was obtained when MnO₂ was synthesized by reducing potassium permanganate using ethanol as a reducing agent under normal temperature and pressure at pH 7 (Method 1). MnO₂ nanowire (Figure 1b) was observed when MnO₂ was prepared via a hydrothermal synthesis under acidic conditions (Method 2). The length of the nanowire is approximately 6–10 µm. The obvious different morphologies were expected to result in different electrochemical performances. The crystal structure of the MnO₂ nanowire (MnO₂-NW) was characterized by X-ray powder diffraction (XRD). In XRD patterns of MnO₂-NW (Figure 1c), the diffraction peaks at 12.78°,18.06°, 28.82°, 37.82° and 42.17° are indexed to crystal Surface of (110), (200), (310), (211) and (301), respectively, which are matched with the standard diffraction pattern of α -MnO₂ (JCPDS card No.44-0141). More importantly, no other impurities are found in these XRD patterns, revealing that as-synthesized MnO₂-NW is well crystallized and at high purity.



Figure 1. SEM of granular MnO₂ (a) and MnO₂-NW (b); XRD of MnO₂-NW (c).

X-ray photoelectron spectroscopy (XPS) was used to study the surface composition of MnO_2 -NW (Figure 2). According to the full scan XPS spectrum (Figure 2a), Mn and O were observed on the surface of the sample of MnO_2 -NW. In the high-resolution spectrum of O 1s (Figure 2b), the peak at 529.88 eV corresponded to lattice oxygen, and the appearance of a high-intensity peak indicates that a large amount of lattice oxygen (O latt) was present in MnO_2 nanowires. The characteristic peak of O abs at 531.49 eV was related to surface-adsorbed oxygen, hydroxyl groups, or defect-related oxygen species [36,37]. Figure 2c displays the XPS energy spectrum of Mn 3s. The valence state of Mn was usually determined based on the peak spacing of Mn 3s. The peak spacing of Mn 3s in MnO_2 -NW was 4.70 eV, indicating that most of the Mn in the sample exists in the form of +4 valence. In the XPS spectra of Mn 2p (Figure 2d), the peaks at 642.47 eV and 641.04 eV correspond to Mn^{4+} and Mn^{3+} , respectively. The content of Mn^{3+} is relatively low, indicating that most of the Mn in the form of +4 valence [38,39].



Figure 2. XPS figures of MnO₂-NW. (a) full spectrum, (b) O 1s, (c) Mn 3s, (d) Mn 2p.

3.2. Electrochemical Behavior of TBBPA on MnO₂-NW/CP

Figure 3a shows the cyclic voltammograms of 500 nM TBBPA on CP, MnO_2/CP (MnO_2 nanosheet), and MnO_2 -NW/CP, respectively. The buffer solution was 0.10 M phosphate buffer solution (pH 6.5). As can be seen from Figure 3a, an irreversible oxidation peak at 0.60 V (vs. Ag/AgCl) was found to correspond to the irreversible oxidation of TBBPA at the working electrode surface. The comparison of the oxidation peak current of TBBPA

on the above three electrodes is displayed in Figure 3b. It was shown that the oxidation peak current of TBBPA was slightly enhanced by modifying the nanosheet MnO_2 on CP. In addition, the electrochemical signal of TBBPA on MnO_2 -NW/CP was approximately twice higher than that on the bare CP electrode. Furthermore, the oxidation potential shifted to 0.58 V. It is well understood that the electrochemical activity of nano MnO_2 is shape-dependent. Compared with the MnO_2 nanosheet, the MnO_2 nanowire can provide a higher surface area and more abundant surface oxygen, which can result in enhanced catalytic activity. The oxidation of TBBPA was obviously promoted when the CP electrode was modified by MnO_2 -NW, which may be due to the larger specific surface area, better electrical conductivity and the oxidizing ability of MnO_2 -NW. Hence, MnO_2 -NW/CP was chosen for the detection of TBBPA.



Figure 3. (a) CVs of 500 nM TBBPA on different electrodes; (b) oxidation current of TBBPA on different electrodes; (c) CVs of MnO_2-NW/CP in 2.5 mM K₃[Fe(CN)₆] at different scan rates; (d) The linear plot of K₃[Fe(CN)₆] ipa vs. $v^{1/2}$.

CVs of MnO₂-NW/CP in 0.1 M KCl solution containing 2.5 mM K₃[Fe(CN)₆] at various scan rates were recorded in the range of 30–150 mV/s to investigate the effective electrochemical area of the MnO₂-NW/CP electrode. It was observed that the oxidation and reduction peaks of potassium ferricyanide increase with increasing scanning speed at the MnO₂-NW/CP electrode, and the potential difference between the oxidation and reduction peaks becomes larger. Diffusion-controlled behavior of K₃[Fe(CN)₆] could be deduced from the linear relationship between oxidation peak currents *i*_p and the square root of scan rates $v^{1/2}$ with the regression equation of *i*_p = 0.04109 $v^{1/2}$ – 0.05549 (R² = 0.9976) (Figure 3d). The Randles–Sevcik equation was used to calculate the effective surface area (ESA) [40].

$$i_p = 0.4463nFAC \left(\frac{nFvD}{RT}\right)^{1/2} = 2.69 \times 10^5 n^{2/3} ACD^{1/2} v^{1/2}$$
 (25 °C) (1)

where i_p (A) is the oxidation or reduction peak current; n is the total number of electrons exchanged in the redox reaction; *A* (cm²) is the effective surface area (ESA); *C* (mol/cm³) is the concentration of K₃[Fe(CN)₆] (2.5 mM); *D* (cm²/s) is the diffusion coefficient of [Fe(CN)₆]^{3–} (6.5 × 10⁻⁶ cm²/s); and *v* (V/s) is the scan rate. In our experiment, the slope

was 0.04109, and the ESA value was calculated as 0.24 cm^2 . The ESA value of the bare carbon paper electrode was determined using a similar process to be 0.026 cm². Thus, the ESA of MnO₂-NW/CP was about nine times greater than that of a bare carbon paper electrode, suggesting the excellent electrochemical properties of MnO₂-NW/CP.

Figure 4a shows CVs of MnO₂-NW/CP in 0.1 M pH 6.5 phosphate buffer solutions containing 500 nM TBBPA at different scan rates in the range of 25–150 mV/s. The peak current in CVs is coupled with the change of concentration gradient with time. Thus, the peak currents are obviously influenced by the scan rate. This is because the scan rate determines the time between the switching potential and the peak potential. It was shown that the oxidation peak currents of TBBPA kept increasing with the increase in the scan rate in the range of 25–150 mV/s. Figure 4b shows a plot of the TBBPA oxidation peak current versus sweep rate with the linear equation $i_p = 0.0975v + 0.00459$ (R² = 0.9915). Figure 4c is a plot of i_p versus $v^{1/2}$ with the linear equation $i_p = 1.67755v^{1/2} - 6.61462$ (R² = 0.9531). The oxidation peak currents of TBBPA were background subtracted to correct for the larger charging current contribution at the higher scan rate. The oxidation peak current of TBBPA is proportional to the potential scan rate, which is in accordance with the formula of $i_p = (n^2 F^2 \Gamma AV)/(4RT)$. Moreover, the independence between i_p and the square root of the scan rate reveals that the oxidation of TBBPA on MnO₂-NW/CP was not controlled by the diffusing process. Thus, TBBPA oxidation on a MnO₂-NW/CP is an adsorption-controlled process. The oxidation peak potentials of TBBPA were found to shift toward positive potentials with the increase in scan rates, which is related to the irreversible oxidation process of TBBPA.



Figure 4. (a) CVs of 500 nM TBBPA in 0.1 M pH 6.5 PBS on MnO₂–NW/CP at different scan rates; (b)The linear plot of i_p vs. v; (c)The linear plot of i_p vs. $v^{1/2}$.

3.3. Optimization of Experimental Conditions

DPV was chosen to prepare a sensitive sensor for the determination of TBBPA. The experiment parameters, including the pH value of the buffer solution, the enriching time and the amount of MnO_2 -NW, were optimized by recording the electrochemical performance of TBBPA under different experiment conditions.

Figure 5a shows the oxidation peak currents and peak potentials of TBBPA at different pH conditions. It was found that the oxidation peak currents of TBBPA increased with increasing pH in the range of 5.5–6.5 and reached a maximum at pH 6.5. The pKa₁ and pKa₂ of TBBPA were reported to be 7.5 and 8.5. TBBPA was not dissociated when the pH was 6.5. The undissociated TBBPA can be adsorbed more easily on a MnO₂-NW/CP electrode than the dissociated form. This resulted in the maximum oxidation peak current of TBBPA at pH 6.5. Hence, pH 6.5 was chosen as the optimum pH condition in the subsequent experiments. In the pH range of 5.8–8.0, the oxidation peak potential of TBBPA negatively linearly shifted with an increase in pH value following the equations of Ep = 0.978–0.0594 pH. This shows that protons took part in the electrochemical reaction of TBBPA. The slope -0.0594 V/pH was close to the value obtained from the Nernst equation (-0.059 V/pH), which indicated that the number of electrons was equal to the number of protons during the oxidation of TBBPA [41]. Referring to the oxidation mechanism



of TBBPA on Fe₃O₄@SiO₂@CDs-CTAB/GCE [20], the oxidation mechanism of TBBPA on MnO_2 -NW/CP is deduced in Figure 6.

Figure 5. (**a**) The effect of pH on the oxidation peak current and potential of TBBPA; (**b**) The effect of enrichment time on the peak current of TBBPA; (**c**) The effect of MnO₂-NW amount on the peak current of TBBPA.



Figure 6. Electrochemical oxidation mechanism of TBBPA.

The effect of enrichment time on the oxidation peak current at the open circuit of TBBPA (500 nM) is shown in Figure 5b. When the enrichment time was less than 5 min, the peak current increased rapidly with the increase in enrichment time. This is because more TBBPA was adsorbed on the MnO₂-NW/CP electrode with increasing enrichment time. When the enrichment time was above 5 min, the oxidation peak current tended to be stable due to the adsorption saturation of TBBPA. Therefore, 5 min of enrichment time was chosen.

The effect of the modification amount of MnO_2 -NW was investigated in Figure 5c. It was found that the oxidation current of TBBPA increased sharply when the modification amount of MnO_2 -NW suspension increased from 3.0 to 7.0 µL. This might be a result of more catalyst-enhanced catalytic ability. However, when the modification amount was over 7.0 µL, the oxidation peak current decreased due to the deterioration of electrical conductivity. Therefore, 7.0 µL suspension of MnO_2 -NW was selected as the optimal modification amount in this work.

3.4. Electrochemical Detection of TBBPA

DPV of MnO₂-NW/CP in different TBBPA concentrations was investigated under optimal experimental conditions (Figure 7). As shown in Figure 7a, the oxidation currents increased when TBBPA was added successively from 70 to 500 nM. The linear regression equation was $i_p = 0.00323c + 0.06304$, R² = 0.9914 (Figure 7b). The estimated detection limit is 3.1 nM based on a three-signal-to-noise ratio of 3. It could be seen that our electrochemical sensor exhibited a wide linear range and a low detection limit, which might be due to the high ESA of the MnO₂-NW/CP, with plenty of active sites. Our experimental results were compared with the literature reports in Table 1, indicating that this method has some favorable advantages.



Figure 7. (a) DPVs of MnO_2-NW/CP in 0.1 M pH 6.5 PBS containing different concentrations of TBBPA; (b) The corresponding calibration plots between the peak currents and the concentrations of TBBPA.

Table 1. Comparison of the experimental results with other electrodes or methods.

Sensor Assembly	Method	LOD	Linear Range	Reference
CNTs@ZIF-67/PFDA/AB	DPV	4.2 nM	10~150 nM	[19]
AuNPs-PSSA/GCE	DPV	25 pM	0.1~10 nM	[42]
MI-TiO ₂ /Au/rGO	DPV, CV	0.51 nM	1.68~100 nM	[43]
CTAB-MnO ₂ /Pd	I-t	0.17 ng/mL	0~81 ng/mL	[44]
poly(PPBim-DS)/GCE	DPV	20 nM	0.05~10 μM	[39]
MnO ₂ -NW/CP	DPV	3.1 nM	70~500 nM	This work

Five parallel MnO₂-NW/CP electrodes were prepared for the detection of 500 nM TBBPA, and the detection relative standard deviation was 3.8%. One of the above five electrodes was further investigated five consecutive times, and the relative standard deviation was 1.9%. The results showed good reproducibility and precision of MnO₂-NW/CP.

3.5. Real Samples Analysis

To estimate the potential of a MnO_2 -NW for the detection of TBBPA in practical applications, the fabricated electrochemical sensor was employed to detect TBBPA in lake water (Suzhou, China). Before detection, the water was filtered through a 0.45 µm membrane to remove suspended solids. No response to TBBPA was found in these real samples, indicating that the concentration of TBBPA was extremely low or that no TBBPA existed in these real samples. Then standard solutions of TBBPA were spiked into real sample solutions for recovery evaluation. The recoveries were in the range of 94.5% to 100.5%. The results indicated that MnO_2 -NW/CP is reliable and could be applied to detect TBBPA in the actual water sample.

4. Conclusions

In this study, a cost-effective, simple fabricated and sensitive electrochemical sensor was prepared by modifying carbon paper with a MnO_2 nanomaterial. The performance of electrochemical sensors was proven to be closely related to the microscopic morphology of MnO_2 . The fabricated MnO_2 -NW/CP displayed attractive performance for the detection of TBBPA. The sensitivity and stability of MnO_2 -NW/CP were satisfied, and the selectivity of MnO_2 -NW/CP can be further enhanced by combining other materials, such as molecular imprinting technology. It is reasonable to believe that MnO_2 nanowire-based electrochemical sensors might be a promising method for the effective detection of TBPPA in environment monitoring.

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