Molecularly imprinted electrochemical sensor based on nickel nanoparticles–graphene nanocomposites modified electrode for determination of tetrabromobisphenol A

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In this work, a novel imprinted electrochemical sensor based on nickel nanoparticles–graphene modified electrode was developed for the determination of 3, 3',5,5'-tetrabromobisphenol A (TBBPA). The preparation procedure of imprinted electrode was discussed. The electrochemical characteristics of the imprinted sensor were investigated using cyclic voltammetry and electrochemical impedance spectroscopy in detail. The response currents of the imprinted electrode exhibited a linear relationship toward TBBPA concentrations ranging from $5.0 \times 10^{-10}$ to $1.0 \times 10^{-5}$ mol L$^{-1}$ with the detection limit of $1.3 \times 10^{-9}$ mol L$^{-1}$ (S/N = 3). The developed electrochemical imprinted sensor was applied to the direct determination of TBBPA in tap water, rain and lake water samples using standard addition method successfully.

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1. Introduction

Tetrabromobisphenol A (TBBPA), one of the widely used brominated flame retardants, is utilized as a reactive additive in polymerization widely [1]. However, TBBPA in the resins is easy to leak into the environment which was reported to be toxic to primary cultured cerebellar granule neurons [2]. Indeed, TBBPA has been found in sediments, sewage sludge, wildlife and human serum [3]. Various approaches have been proposed for TBBPA detection, such as gas chromatography tandem mass spectrometry (GC-MS) [4], solid-phase extraction with high-performance liquid chromatography tandem mass spectrometry (HPLC-MS) [5], solid-phase extraction with gas chromatography tandem mass spectrometry (SPE-GC-MS) [6], high-performance liquid chromatography spectrometry tandem mass spectrometry tandem mass spectrometry (HPLC-MS-MS) [7] and other complicated techniques [8,9]. However, applications of these methods are limited by the expensive instrument, high cost and complicated pretreatment procedures. While electrochemical sensor possessing the advantages of excellent sensitivity, rapid response, simplicity, low cost and in vivo detection, has been applied in medical, biological and environmental analysis extensively [10]. However, a little endeavor has been devoted to fabricate an electrochemical sensor for TBBPA determination [11]. Therefore, it is interesting to develop an electrochemical sensor for TBBPA determination with high sensitivity and selectivity.

Molecularly imprinted polymer (MIP) has proven to be an efficient recognition element due to the advantages of stability and selectivity for the template recognition [12,13]. For the past years, various materials involving conductive pyrrole polymer, graphene (GP) and metal nanoparticles have been employed for electrode modification aiming at enhancing the sensitivity and selectivity of the imprinted electrochemical sensor [14,15]. Graphene, emerging as a new two-dimensional single layer carbon material, has achieved extensive attention of scientists due to its specific properties of high electrical conductivity. Nickel nanoparticles have been extensively used in electrode modification on account of its extraordinary catalytic activities and high conductivities [16]. Many molecularly imprinted electrochemical sensors based on nickel nanoparticles and graphene hybrids were also fabricated for substance analysis, such as for sunset yellow and glucose [17–19]. Indeed, the combination of graphene and nickel nanoparticles with imprinted technique provides an attractive route to fabricate imprinted sensor with appreciative sensitivity and selectivity [20]. However, the commonly reported approaches for preparation of graphene modified electrodes are applying merely a simple physical assembly or sol–gel route, which are facing some drawbacks [17–19,21,22].
In this paper, we describe a novel TBBPA imprinted electrochemical sensor based on nickel nanoparticles and graphene hybrids modified carbon electrode for TBBPA direct assays. Graphene covalently modification on carbon electrode surface by diazonium salt reaction [23] and the electrochemical deposition of nickel nanoparticles were discussed in detail. Each modification procedure and the performance of the imprinted sensor were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in detail. The method provides a novel efficient protocol for the ultrasensitive detection of TBBPA in water environment.

2. Experimental

2.1. Material and methods

Graphite powder, KMnO₄, H₂SO₄, Bu₄NBF₄, HBF₄ (50 wt% in water), HCl, diethyl ether (Et₂O), acetonitrile, potassium ferrocyanide and 30% H₂O₂ aqueous solutions were all analytical grade and obtained from Beijing Chemical Reagents Company. NiSO₄ and Ni(NO₃)₂ were obtained from Aladdin Reagent Company (Shanghai, China). 3, 3', 5, 5'-Tetrabromobisphenol A (TBBPA), tetrabromo bisphenol S (TBBPS) and bisphenol A (BA) were obtained from Alfa Aesar Company (Tianjin, China).

All electrochemical experiments were carried out on a CHI660B electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) using a three-electrode system, where a saturated calomel electrode (SCE) served as the reference electrode, a platinum wire electrode as the auxiliary electrode and modified carbon electrode as the working electrode. The concentration of Fe(CN)₆³⁻/⁴⁻ acting as probe used in the electrochemical characterization is 1.0 × 10⁻³ mol L⁻¹ in this experiment. Morphology characterization was carried out on a scanning electron microscope (JEOL, JSM-6700F) at 15 kV.

2.2. Synthesis of 4-nitrobenzenediazonium tetrafluoroborate salt

4-Nitrobenzenediazonium tetrafluoroborate salt (NBT) was synthesized according to the reported literature [24] and the detail procedure was shown in Fig. 1. Briefly, 4.0 mmol of 4-nitroaniline was added in the mixture solution of 1.5 mL HBF₄ (50%, 12 mol) and 4.0 mL water. After that, the solution was cooled in ice bath for 15 min. Then 4.3 mmol of NaNO₂ (dissolved with water) was added dropwise into the acidic aniline solution under stirring and allowed to react for 40 min. When a precipitate appears, the solution was filtered and washed with diethyl ether. The NBT was purified by recrystallization (dissolving in minimum amount of acetonitrile and adding excess amount of cold ether). Finally, the purified NBT was dried under vacuum overnight and stored at -20 °C.

2.3. Preparation of TBBPA imprinted sensor

The TBBPA imprinted sensor was prepared according to the following steps and the detail procedures were illustrated in Fig. 1. Prior to surface modification, the home-made bare carbon electrode with size of 5 × 3 mm was polished with 1 and 0.05 mm alumina slurries and finally washed with water. Amine-terminated benzenediazonium modified carbon electrode (NBD/CE) was prepared and the details were as follow. Firstly, NBT was electrochemically

![Fig. 1. Detailed procedure diagrams for fabrication of the MIP/Ni/GP/CE sensor and the chemical structure of TBBPA, TBBPS and BPA.](image-url)
deposited onto the cleaned CE applying cyclic voltammetry (CV) which was conducted from -0.3 to -1.8 V vs. SCE with a scan rate of 50 mV s⁻¹ for three cycles in the mixture acetonitrile solution of 2.0 × 10⁻³ mol L⁻¹ NBT salt and 0.1 mol L⁻¹ Bu₄NBF₄. After electrodeposition, the electrode was rinsed repeatedly with acetonitrile and water to elute the physically adsorbed NBT. Then, nitro groups were electrochemically reduced to amine groups by CV scanning under the potential range of -0.4 V ~ -1.6 V vs. SCE at 50 mV s⁻¹ for three cycles in a 10% ethanol solution containing 1.0 mol L⁻¹ KCl and rinsed with water. Next, the NBD/CE was immersed in 1.0 mL of diluted solution of graphene oxide (0.5 mg mL⁻¹) containing HCl (0.5 mol L⁻¹) and NaNO₂ (12 mg) for 4 h to obtain graphene oxide modified electrode (GO/CE), and followed by washed with water and dried under room temperature (RT). After that, the electrochemical reduction of graphene oxide to graphene was conducted using CV scanning with a potential of 0 ~ -1.3 V vs. SCE at a scan rate of 50 mV s⁻¹ for three cycles in 1.0 mol L⁻¹ KCl solution using GO/CE as the working electrode. Then the resulting graphene modified electrode (GP/CE) was washed with water and dried under RT for further use. Finally, nickel nanoparticles were electrochemically deposited on the GP/CE using chronopotentiometry method in 0.2 mol L⁻¹ Na₂SO₄ aqueous solution containing 2.5 × 10⁻² mol L⁻¹ Ni(NO₃)₂ and 2.5 × 10⁻² mol L⁻¹ NiSO₄. Chronopotentiometry method was performed with potential from -0.1 to 0.4 V vs. SCE and a cathode current density of 0.05 mA cm⁻² for 120 seconds. Hence the obtained modified electrode is denoted as Ni/CE.

The TBBPA imprinted film electrodeposited onto the Ni/CE was conducted using CV scanning between 0 and 0.85 V vs. SCE with a scanning rate of 50 mV s⁻¹ for nine cycles in the presence of 0.2 mol L⁻¹ pyrrole phosphate buffer solution (pH 7.0) containing 5.0 × 10⁻³ mol L⁻¹ TBBPA. Finally, the imprinted electrode was immersed into ethanol solution containing 20% of acetic acid for 1 h to remove the template.

2.4. Sample preparation

All water samples involving tap water, rain and lake water samples were collected in Jishou city of Hunan province during September–October 2012. The samples were filtered with 0.45 μm membrane. After filtration, the samples were prepared with PBS buffer (pH 7.0) and then a certain number of TBBPA was added. These samples were stored in sealed containers at 0 ~ 4 °C until analysis.

3. Results and Discussion

3.1. Preparation of TBBPA molecularly imprinted sensor

The preparation procedures of the TBBPA imprinted sensor were shown in Fig. 1. For the immobilization of graphene oxide on the chemically modified CE surface, 4-nitrobenzenediazonium tetrafluoroborate salt (NBT), which was prepared in situ, was bound onto the CE surface (Fig. 1a). Then, the amine groups obtained by electrochemical reduction of nitro groups [25] are converted into the corresponding diazonium, which covalently bind with graphene oxide. Firstly, NBT was electrodeposited on the CE surface using CV method. As shown in Fig. 2A, there is a sharp irreversible peak at −1.2 V vs. SCE during the first cycle, and the peak currents density diminished strictly in subsequent cycles indicating the successfully modification of NBT. Secondly, the nitro groups on NBT were electrochemically reduced to amine groups by CV electrochemical scanning under the potential range from −0.4 V to −1.6 V vs. SCE at 50 mV s⁻¹ in a 10% ethanol solution containing 1.0 mol L⁻¹ KCl (the electrode was referred as NBD/CE). The resulting cyclic voltammograms (shown in Fig. 2B) shows a sharp irreversible peak at −1.05 V vs. SCE during the first cycle, followed by greatly diminished currents density in subsequent cycles. After that, graphene oxide was covalently modified on the NBD-modified CE surface.

![Fig. 2. Cyclic voltammograms for (A) electrodeposition of NBD (2 × 10⁻³ mol L⁻¹ NBD salt with 0.1 mol L⁻¹ Bu₄NBF₄ in acetonitrile solution) on CE surface, (B) electrochemical reduction of the nitro groups of NBD to amine groups in a 10% ethanolic solution of 1.0 mol L⁻¹ KCl and (C) electrochemical reduction of GO/NBD/CE in 0.5 mol L⁻¹ NaCl solution at a scan rate of 0.05 V s⁻¹. (D) Chronopotentiometry response of deposition of nickel nanoparticles performed in 0.2 mol L⁻¹ Na₂SO₄ aqueous solution containing 2.5 × 10⁻² mol L⁻¹ Ni(NO₃)₂ and 2.5 × 10⁻² mol L⁻¹ NiSO₄.](image-url)
attributing to the diazonium salt reaction (the electrode was referred as GO/CE). Then the graphene oxide modified on the GO/CE was electrochemically reduced by cyclic voltammetry scanning from 0 to -1.3 V vs. SCE and a sharp reduction peak was observed at -0.94 V vs. SCE during the first cycle, followed by greatly diminished currents density in subsequent cycles (shown in Fig. 2C). This electrochemical behavior is similar to the previously reported for the electrochemical reduction of graphene oxide sheets [25,26], which indicated that the reduction of the graphene oxide was conducted. After the electrochemical reduction of graphene oxide, nickel nanoparticles were electrodeposited onto the GP/CE surface using chronopotentiometry technique in 0.2 mol L⁻¹ Na₂SO₄ solution containing 2.5 × 10⁻² mol L⁻¹ Ni(NO₃)₂ and 2.5 × 10⁻² mol L⁻¹ NiSO₄. As shown in Fig. 2D, the potential increased quickly and arrived to balance after 20 seconds, which was conformed with chronopotentiometry response of the metal deposition[27]. In order to obtain a higher density of nickel nanoparticles, chronopotentiometry was conducted for 120 seconds. The phenomenon can be explained by that Ni²⁺ ion in the electrolyte diffused to the GP/CE surface and electrochemically reduced to nickel crystal nuclei. The nickel crystal nuclei regenerating nickel nanoparticles quickly with further deposition resulted in potential signal measurement decrease at the GP/CE (as showed in Fig. 2D). While the regeneration reaction proceeds an additional strip process of Ni²⁺ species occurred simultaneously. Thus the chronopotentiometry curve reaches to stabilize over time (the electrode was referred as Ni/GP(CE) [28]. After electrochemical deposition of nickel nanoparticles, pyrrole polymer (PPy) film was deposited onto the Ni/GP(CE) electrode surface by electrodeposition technique to obtain MIP/Ni/GP/CE. Briefly, cyclic voltammetry scanning in the potential of 0 ~ 0.85 V vs. SCE was conducted for 10 cycles in 0.2 mol L⁻¹ pyrrole phosphate buffer solution (pH 7.0) containing 5.0 × 10⁻³ mol L⁻¹ TBBPA. Fig. 3 shows the cyclic voltamograms of pyrrole electrochemical deposition on the electrode. As shown in Fig. 3, the currents density decreased with the increment of CV cycles, which indicated the imprinted film was deposited on the electrode surface successfully. The currents density of subsequent cycles decreased due to TBBPA molecules were trapped into the pyrrole matrix polymer during the polypyrrole electropolymerization process, which increased the electron transfer difficulties to the electrode. After scanning nine cycles, the current density changes slightly. Thus, the optimum CV scanning cycle was selected for nine cycles to form a proper imprinted layer on the electrode surface. Finally, the imprinted electrode was rinsed with ethanol solution containing 20% of acetic acid for 1 h to remove the template TBBPA.

3.2. Characterization

The morphologies of the carbon electrodes at different modification processes in this study were characterized by scanning electron microscope (SEM) and the results were shown in Fig. 4. A smooth surface was observed for the bare carbon electrode
Electrochemical impedance spectroscopy (EIS) is an effective technique for probing the features of modified electrodes. The typical impedance spectrum includes a semicircle portion and a linear portion. The semicircle diameter at higher frequencies corresponds to the electron-transfer resistance (Rct), and the linear part at lower frequencies corresponds to the diffusion process [30]. Fig. 6 represents the EIS of Ni/GP/CE (Fig. 6a), MIP/Ni/GP/CE without elution (Fig. 6b) and MIP/Ni/GP/CE after TBBPA removed (Fig. 6c) in the presence of $1.0 \times 10^{-3}$ mol L$^{-1}$ Fe(CN)$_6^{3-/4-}$. As shown in Fig. 6a, a typical impedance spectra involving the semicircle diameter at higher frequencies and a 45° liner was observed for Ni/GP/CE in $1.0 \times 10^{-3}$ mol L$^{-1}$ Fe(CN)$_6^{3-/4-}$ solution, which indicated a solution diffusion control procedure. After an electrochemical imprinted film was electrodeposited onto the Ni/GP/CE, as shown in Fig. 6b, the semicircle diameter increased, which was ascribed to the covering of the imprinted pyrrole polymer. When the template TBBPA was removed from the surface of the MIP/Ni/GP/CE, as shown in Fig. 6c, the electron transfer resistance was smaller than that of MIP/Ni/GP/CE without elution, which was due to the elution of the template TBBPA molecule resulting in increment of the electron transfer rate.

The conductivities of different electrodes involving Ni/GP/CE, MIP/Ni/GP/CE without elution and MIP/Ni/GP/CE after elution were also discussed by the impedance spectroscopy in the presence of $1.0 \times 10^{-3}$ mol L$^{-1}$ Fe(CN)$_6^{3-/4-}$. These Nyquist plots were fitted by an equivalent circuit in the inset of Fig. 6, and the fitting values including $R_b$ (the intersection of the curve at real part $Z'$ at the high frequencies range), $R_{ct}$ (the semicircle at high frequencies), $C$ (the double-layer capacitance) and the Warburg impedance (W) for the stepwise assembled layers on the electrode of electrochemical impedance spectroscopy were presented in Table 1. The Ni/GP/CE exhibits values of $R_b$ (3.8 ohm cm$^2$), $R_{ct}$ (14.0 ohm cm$^2$ calculated by the instrument), $C$ (0.056 µF) and W (0.002). After electrodeposition polypyrrole membrane, the semicircle of the MIP/Ni/GP/CE increased dramatically and the electron transfer resistance reduced to 58.0 ohm cm$^2$, while the double-layer capacitance increased ($C = 0.156$ µF), which is due to the coating of polypyrrole membrane. When the elution TBBPA step was conducted, the semicircle diameter and double-layer capacitance of the imprinted electrode decreased further ($R_b = 28.0$ ohm cm$^2$, $C = 0.091$ µF), contributing to the successfully elution of TBBPA template. The phenomena can be explained by that the capacitance of the membrane decreased

![Fig. 5. Cyclic voltammograms for (a) bare electrode, (b) graphene oxide modified electrode surface (GO/CE), (c) graphene modified electrode surface (GP/CE), (d) graphene modified electrode surface electrode surface after deposited nickel nanoparticles (Ni/GP/CE), (e) MIP/Ni/GP/CE electrode surface in 1.0 × 10$^{-3}$ mol L$^{-1}$ Fe(CN)$_6^{3-/4-}$ PBS (pH 7.0) at scan rate of 0.05 V s$^{-1}$.](image)

![Fig. 6. Electrochemical impedance spectroscopy of (a) GP/CE, (b) MIP/Ni/GP/CE without elution and (c) MIP/Ni/GP/CE after NP removed in the presence of 1.0 × 10$^{-3}$ mol L$^{-1}$ of Fe(CN)$_6^{3-/4-}$. Inset: equivalent electrical circuit diagrams for impedance plots. $R_b$ (the intersection of the curve at real part $Z'$ in the high frequencies range), $R_{ct}$ (the semicircle at high frequencies), $C$ (the double-layer capacitance) and the Warburg impedance (the slope of the curves at a low frequency).](image)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Fitted impedance values for the imprinted carbon electrode. $R_b$ (the intersection of the curve at real part $Z'$ at the high frequencies range), $R_{ct}$ (the semicircle at high frequencies), $C$ (the double-layer capacitance) and the Warburg impedance (the slope of the curves at a low frequency).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrodes</td>
<td>$R_b$(ohm cm$^2$)</td>
</tr>
<tr>
<td>GP/CE</td>
<td>14.0</td>
</tr>
<tr>
<td>MIP/GP/CE without elution</td>
<td>58.0</td>
</tr>
<tr>
<td>MIP/GP/CE after elution</td>
<td>28.0</td>
</tr>
</tbody>
</table>

$R_b$ (the intersection of the curve at real part $Z'$ at the high frequencies range), $R_{ct}$ (the semicircle at high frequencies), $C$ (the double-layer capacitance) and the Warburg impedance (W).
3.3. Influence of the scan rate on the electrochemical properties of MIP/Ni/GP/CE

The electrochemical behavior of the MIP/Ni/GP/CE toward TBBPA was investigated using cyclic voltammetry in detail. Fig. 7 shows the cyclic voltammograms of MIP/Ni/GP/CE in 0.1 mol L⁻¹ PBS (pH 7.0) containing 1.0 × 10⁻⁷ mol L⁻¹ TBBPA with different scan rates ranging from 0.005 to 0.08 V s⁻¹. It is clear that the peak currents density enhanced with increasing the scan rate. In particular, the CV curves were unsmooth when the scan rate was over 0.08 V s⁻¹. Therefore, the optimized scan rate was optimized at 0.05 V s⁻¹. As can be seen in the inset of in Fig. 7, both the oxidation (iₚa) and reduction peak currents density (iₚc) were linearly proportional to the square root of scan rate (ν¹/²) ranging from 0.005 to 0.08 V s⁻¹, suggesting that the electrode reaction of TBBPA on MIP/Ni/GP/CE corresponds to a diffusion-controlled process [32]. The regression equations are as follow:

\[
iₚa = 4.096ν^{1/2} - 0.295(R^2 = 0.98) \quad (1)
\]

\[
iₚc = -2.784ν^{1/2} + 0.190(R^2 = 0.97) \quad (2)
\]

The relationship between the peak potentials (Eₚ) and the logarithm value of scan rates (log ν) was also studied and the results were shown in Fig. 8. With the increase of scan rate, the oxidation peak potentials shifted positively and the reduction peak potentials shifted negatively. When ν > 0.01 V s⁻¹, the Eₚa and Eₚc were linearly dependent on the log ν with the regression equations as follow:

\[
Eₚa = 0.100\log \nu + 0.606(R^2 = 0.99) \quad (3)
\]

\[
Eₚc = -0.045\log \nu + 0.254(R^2 = 0.99) \quad (4)
\]

The charge transfer coefficient (α) was calculated to be 0.310 according to Laviron theory [33] that a plot of Eₚ versus log ν yields two straight lines with slopes of −2.3RT/αnF and 2.3 RT/(1 − α)nF for the reduction peak and oxidation peak, respectively. When ν is approach to zero, both the oxidation and reduction peaks are closed to reversible peaks with nearly symmetrical shape (shown in the inset of Fig. 8). The difference between Eₚa and Eₚc (0.066 V vs. SCE) becomes independent of α and tends towards 56.5/nα. Thus, 

\[nα\text{ was calculated to be 1, indicating that one electrons are involved in the electrochemical redox process of TBBPA.}

3.4. Calibration curve

In order to study the analytical capabilities of the developed imprinted sensors, a series of samples possessing different TBBPA concentrations were investigated using differential pulse voltammetry (DPV) and the results were recorded in Fig. 9. The imprinted electrode was immersed into ethanol solution containing 20% of acetic acid for 20 min after each detection process to remove the template. As depicted in Fig. 9, a peak current density signal at 0.37 V vs. SCE was obtained and the peak currents density increased with the increment of TBBPA concentrations. Since TBBPA could not occurring electrochemical reaction on the imprinted graphene modified electrode unless Fe(CN)₆³⁻/⁴⁻ probe being added which has been reported in our previous work [11]. Thus, the response mechanism can be explained that the TBBPA molecules diffuse to the electrode combining with the imprinted cavities, in which Fe(CN)₆³⁻/⁴⁻ acting as probe cross through and take place oxidation-reduction reaction on the carbon electrode surface. Thus the more the TBBPA combined with the imprinted cavities, the more the current density responded of the imprinted carbon electrode. A linear relationship between the response currents density (Ipc) toward the TBBPA concentrations (C) ranging from 5.0 × 10⁻¹⁰

\[\text{Current Density (mA cm}^{-2}\text{)} = 0.100\log C + 0.606 \quad (5)
\]

\[\text{Current Density (mA cm}^{-2}\text{)} = -0.045\log C + 0.254 \quad (6)
\]
to $1.0 \times 10^{-5}$ mol L$^{-1}$ was obtained. As shown in the inset of Fig. 9, the linear regression equation is as follows:

$$
\text{Ipc} = 2.163 + 0.119 \log C_{\text{TBBPA}} \text{(mol L}^{-1}) (R^2 = 0.99).
$$

The determination limit of the imprinted electrode is calculated as $1.3 \times 10^{-10}$ mol L$^{-1}$ ($S/N = 3$). Compared with our previous papers on an indirect method for TBBPA detection implemented by monitoring the peak current density of Fe(CN)$_6^{3-}$-TBBPA complex [11], the linear range and detection limit of the developed novel MIP/Ni/GP/CE in this work were improved owing to directly determination of TBBPA. Furthermore, compared with the previous reports using gas chromatography–mass spectrometry and gas chromatography–electron capture negative ionization mass spectrometry to detect TBBPA [34,35], the linear range and detection limit of the developed imprinted sensor were better, which provides a novel electrochemical assay method for direct determination of trace TBBPA in solution.

3.5. Interference, reproducibility and stability of the imprinted sensor

In order to investigate the selectivity of the TBBPA imprinted sensor, some chemical species involving tetrabromo bisphenol S (TBBPS) and bisphenol A (BA) (their structures were shown in Fig. 1) were chosen as interferences due to their structural similarity and interaction types. Fig. 10 shows the DPV results obtained in the determination of $1.0 \times 10^{-9}$ mol L$^{-1}$ TBBPA, TBBPS and BA, respectively. As shown in Fig. 10, the current density signal value toward TBBPS is 0.168 mA cm$^{-2}$, which is 15 and 11 times of that toward TBBPS and BA, respectively. The results showed the imprinted electrode possessed good selectivity. The phenomenon is attributed to the specific structure of the molecularly imprinted polymer matrix. The template TBBPA molecules could enter the imprinted cavities and combine with appropriately conducting oxidation reaction. However, the non-template molecules could not bind with the specific imprinted cavities effectively. These results indicated the high selectivity of the imprinted electrochemical biosensor.

The reproducibility of the imprinted sensor was investigated by assaying $1.0 \times 10^{-9}$ mol L$^{-1}$ TBBPA PBS (pH 7.0) solution with DVP method using three imprinted sensors prepared with the same procedure. A recovery standard deviation (RSD) of 4.2% was obtained, indicating a good sensor-to-sensor reproducibility. Moreover, the reproducibility of the imprinted sensor was examined toward $1.0 \times 10^{-9}$ mol L$^{-1}$ TBBPA for five successive runs; the RSD is 4.0%. To ensure stability, the sensor was stored dry in a refrigerator (4°C) when not in use. The results showed that, after 15 days, the DVP response of the same imprinted sensor to $1.0 \times 10^{-9}$ mol L$^{-1}$ TBBPA decreased only 3.5% compared with the initial response.

3.6. Applications

To further demonstrate its potential in practical applications, the novel imprinted sensor was applied to the detection of TBBPA which was added respectively in tap water, rain and lake water samples. The assay of TBBPA in different samples was conducted with the MIP/Ni/GP/CE according to the proposed method for three times and the results showed in Table 2. As shown in Table 2, the results showed that the MIP/Ni/GP/CE was capable of detecting TBBPA with a good average recovery of 100.3%, 101.0% and 104.0% for three measurements in tap, rain and lake water, respectively, which validated the good recovery and practicability of the developed imprinted sensor.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Added ($\times 10^{-9}$ mol L$^{-1}$)</th>
<th>Found ($\times 10^{-9}$ mol L$^{-1}$)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
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<tbody>
<tr>
<td>Tap water</td>
<td>1.00</td>
<td>1.02</td>
<td>101</td>
<td>4.8</td>
</tr>
<tr>
<td>Rain water</td>
<td>5.00</td>
<td>5.13</td>
<td>103</td>
<td>4.6</td>
</tr>
<tr>
<td>Lake water</td>
<td>1.00</td>
<td>1.03</td>
<td>103</td>
<td>3.7</td>
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<tr>
<td>Tap water</td>
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<td>5.20</td>
<td>104</td>
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<tr>
<td>Lake water</td>
<td>10.00</td>
<td>10.45</td>
<td>105</td>
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</table>

4. Conclusions

A novel imprinted electrochemical sensor based on electrochemical reduced nickel nanoparticles and graphene hybrid covalently modified carbon electrode was developed for direct determination of TBBPA. The developed electrochemical imprinted sensor showed high sensitivity and selectivity toward TBBPA with a detection limit of $1.3 \times 10^{-10}$ mol L$^{-1}$. The high sensitivity of the imprinted sensor was attributed to the enhanced electrochemical property of nickel nanoparticles and graphene hybrid modified surface. In particular, the platform offers the advantages of simplicity, efficiency, and specific assay in target detection, which is essential for TBBPA detection. This work might provide a general protocol to fabricate nickel nanoparticles and graphene hybrid modified chemical sensors for sensitive and selective persistent environmental pollutants detection.

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