Polypyrrole Composite Film for Highly Sensitive and Selective Electrochemical Determination Sensors

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ABSTRACT

In this paper, polypyrrole (PPy) and benz[a]anthracene-7,12-dione (BaD) were electro-polymerized onto a pyrolytic graphite electrode (PGE), constructing a novel BaD/PPy/PGE platform for electrochemical sensing. The morphology and electrochemical properties of the fabricated BaD/PPy/PGE were characterized by scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. Furthermore, the electrochemical behavior of benzo[k]fluoranthene (BkF) at the BaD/PPy/PGE was investigated. Due to the specific interactions between BkF and BaD, a wide linear range of BkF detection from $1.0 \times 10^{-12}$ to $1.0 \times 10^{-9}$ M with good linearity ($R^2 = 0.9962$) and a low detection limit ($1.0 \times 10^{-11}$ M, S/N = 3) were demonstrated. Importantly, other similar aromatics which had one ring or more than two rings, such as benzo[a]anthracene, benzo[a]pyrene, pyrene, benzo[g|h|i]perylene, anthracene, phenanthrene, naphthalene and parachlorophenol, showed insignificant interference on BkF detection. Consequently, this novel BaD/PPy/PGE with excellent stability and selectivity holds promise as an effective BkF electrochemical sensor in aqueous solution. As an example for its practical application, the newly developed sensor was applied to quantitative determination of BkF in waste water samples obtained from a coking plant with satisfactory sensitivity, selectivity, and reversibility.

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1. Introduction

As a group of organic pollutants with strong mutagenicity and carcinogenicity, polycyclic aromatic hydrocarbons (PAHs) are extensively distributed in nature [1–3]. Some PAHs have been demonstrated to disrupt sex hormones, affect immune competence of organisms, and pose reproductive and developmental toxicity as well as skin defects in animals. Thus, it is important to detect and degrade PAHs in an efficient and harmless way. So far, several analytical strategies have been reported for the detection of PAHs, such as chromatography and hyphenated techniques [4–8], fiber optic sensors [9,10] and spectroscopy [11–13]. Although the obtained results are promising, these methods require either expensive instruments or long measuring time and complicated operation. Hence these methods are not suitable for monitoring a large number of samples. Thanks to the low price, high accuracy, and rapid analysis time, electrochemical methods may be the most promising techniques for the detection of PAHs, including electrochemical biosensors [14,15], electrochemical oxidation [16–19] and electroluminescent technology [20]. However, the instability and inactivation problems, poor selectivity and anti-jamming capability of these electrochemical methods have not been addressed. Therefore, it is of great importance to develop a stable, selective and sensitive electroanalytical method for the determination of PAHs, especially for the carcinogenic PAH - benzo[k]fluoranthene (BkF).

In particular, many anthraquinone derivatives with redox activity [21], such as benz[a]anthracene-7,12-dione (BaD) which has a polycyclic structure, can be used as probes in constructing electrochemical sensor of the detection of PAHs based on their interactions with PAHs. Recently, the introduction of conductive polymers has been demonstrated to be able to significantly improve the electrochemical performance of electrodes. Especially, polypyrrole (PPy) has received considerable attention due to its good electrical conductivity, high energy storage capacity and excellent environmental stability [22]. So far, PPy prepared by electrochemical or chemical polymerization methods has been widely applied in electrocatalysis [23–26] and electroanalysis [27–30]. In our
previous work, a conductive PPy membrane with good electrochemical properties was successfully prepared. However, the application of PPy to the electrochemical detection of BkF with BaD as the probe molecule has not been reported.

In this paper, based on the unique $\pi-\pi$ interaction [31] between PAHs and BaD, a sensitive and selective sensing platform to determine BkF using BaD/PPy modified electrode was developed similar to antibody-antigen recognition system. The BaD/PPy modified pyrolytic graphite electrode (PGE) was extensively characterized by scanning electron microscope (SEM), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). In addition, differential pulse voltammetry (DPV) was employed to determine the linear range and detection limit of BkF. Compared with the chromatography and hyphenated techniques, the developed electrochemical sensor is of great advantage because of more sensitive, selective detection, simpler operation, and lower detection limit.

2. Experimental

2.1. Chemicals

All chemicals were used as received without further purification. The structures of PAHs were shown in Scheme 1. BkF, benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), pyrene (PYR), benzo[ghi]perylene (BPE), anthracene (ANT), phenanthrene (PHE), naphthalene (NAP), pyrrole monomer, and $p$-chlorophenol were purchased from Aladdin Reagent Co., Ltd. BaD used in this work was purchased from Afar-Sally Chemical Co., Ltd. (China). The analyzed 16 kinds of PAHs were NAP, acenaphthylene (ANY), ace-naphthene (ANA), fluorine (FLU), PHE, ANT, fluoranthene (FLT), PYR, BaA, chrysene (CHR), benzo[ghi]fluoranthene (BbF), BkF, BaP, indeno[123-cd]pyrene (IPY), dibenzo[a,h]anthracene (DBA), and BPE respectively. Standard PAH solutions were purchased from Accu-Standard, Inc. Each PAH standard solution was diluted by ethanol into a stock solution containing 1.0 mM PAH.

Other chemicals used were of analytical reagent grade and the solutions were prepared with ultrapure water.

2.2. Preparation of the modified electrode

The BaD/PPy/PGE was prepared according to the following procedure: First, the PGE surface was rubbed on an emery paper, washed with duplicate distilled water and softly touched on a piece of weighing paper. Second, 10 mL 0.25 M H$_2$SO$_4$ solution containing 0.01 M pyrrole monomer and 0.5 mM BaD was taken as bulk solution for electrochemical polymerization, and the solutions were deaerated for 10 min with pure nitrogen prior to electrochemical experiments. Finally, polymerization experiments were carried out on a CHI824C electrochemical workstation (CH Instruments, USA) at a constant potential (0.7 V), utilizing a three-electrode cell.

2.3. Electrochemical experiments

All electrochemical experiments were carried out at 298 K. CV and DPV were performed on a CHI824C electrochemical workstation using PGE ($\Phi=6\,\text{mm}$) as the working electrode, Ag/AgCl electrode as the reference electrode, and platinum wire as the auxiliary electrode. EIS was measured in the frequency region of $10^{-2}$-$10^{-1}$ Hz with a voltage excitation amplitude of 5 mV on a IM6ex electrochemical workstation (ZAHNER, Germany).

The electrochemical measurements were performed in 0.1 M NaAc-HAc solution (pH 5.0) containing PAHs. The electrolyte was deaerated with high purity nitrogen for 10 min before each experiment. The experiment results were recorded after the electrode was renewed by ultrapure water and several CV curves scanning in the blank solution.

3. Results and discussion

3.1. SEM images of the BaD/PPy

The morphology of BaD/PPy on the surface of ITO conductive glass as a function of the polymerization time was investigated by SEM as shown in Fig. 1. As the polymerization time increases, the BaD/PPy shows different structures on the surface. As exhibited in
The immobilized Fig. 1a, stripy BaD/PPy has been deposited on the electrode surface after 30 s, but can not completely cover the electrode surface. After 70 s, BaD/PPy is found to be uniformly distributed on the electrode surface (Fig. 1b). However, further increasing polymerization time results in the formation of aggregates on the electrode surface (Fig. 1c-d).

The electrochemical behavior of BaD/PPy/PGE as a function of the polymerization time was further studied by DPV as exhibited in Fig. 2. As the polymerization time increases, the oxidation peak at the BaD/PPy/PGE is gradually enhanced. However, the peak current increases slowly after 70 s and becomes relatively stable after 100 s. It indicates that the deposition of BaD/PPy on the electrode surface reaches the maximum.

Because the peak current is dependent on the amount of BaD immobilized on the electrode surface, short polymerization time will result in low current response and thus reduce the sensitivity.

Therefore, based on DPV and SEM results, 100 s is chosen as the optimal polymerization time.

3.2. EIS of different electrodes

EIS was employed to study the interface properties of different modified electrodes in 0.1 M KCl solution containing 1.0 mM $[\text{Fe(CN)}_6]^{3-/4-}$ to determine the value of charge-transfer resistance ($R_{ct}$). Fig. 3 shows the EIS plots (exhibited as Nyquist plots) for the redox of $[\text{Fe(CN)}_6]^{3-/4-}$ at bare PGE (a) and BaD/PPy/PGE (b). Obviously, bare PGE exhibited a large semicircle and a straight line in high and low frequency regions, respectively. In contrast, the semicircle of BaD/PPy/PGE in the high frequency region is much smaller, indicating a significantly improvement of the electron transfer resistance of $[\text{Fe(CN)}_6]^{3-/4-}$ by this chemical modification.
It demonstrates that PPy is able to promote the electron transfer of electrode. Ramanavicius [32] reported the EIS of differently modified PPy layers that can be applied in the estimation of equivalent circuits for differently modified and treated PPy layers. In this study, the Randles circuit (the inset plot of Fig. 3) is further chosen to fit the impedance data obtained in the experiments, while $R_s$, $Q$, $R_m$, and $Z_{xy}$ represented the resistance of the electrolyte solution, the double layer capacitance, the charge-transfer resistance and the Warburg impedance, respectively. On the bare PGE, the $R_s$ value in the low frequency region was estimated to be 913.3 $\Omega$ (curve a). The $R_{ct}$ value on the BaD/PPy/PGE was decreased to 108.4 $\Omega$ (curve b), due to the presence of PPy as a conductive polymers that promote the electron transfer of $[\text{Fe(CN)}_6]^{3-/4-}$.

3.3. Electrochemical Properties of BaD/PPy/PGE

CV is the most widely used technique for acquiring qualitative information about electrochemical reactions. Fig. 4 illustrates the CV curves of bare PGE (a), 0.5 M BaD in PPy/PGE (b) and BaD/PPy/PGE (c) in 0.1 M NaAc-HAc solution in the absence of the PAHs (pH 5.0). It can be seen that there is no electrochemical response observed on bare PGE and PPy/PGE, indicating that electrochemical reactions of BaD in the solution phase requires a large activation energy. However, a pair of well-defined redox peaks can be observed in Fig. 4c. The peak potential difference ($\Delta E_{p}$) between the oxidation peak ($-0.30\, \text{V}$) and the reduction peak ($-0.35\, \text{V}$) is 50 mV, indicating a quasi-reversible electrochemical behavior and that the BaD doped into PPy film have stronger electrochemical activity than in the solution phase. This may be due to the increased reactive sites and improved the electron transfer rate induced by the doping of BaD into PPy film which effectively reduces the overpotential of the reaction. Furthermore, successive CV curves of BaD/PPy/PGE were recorded and there are no obvious changes in the shape of the CV curves after several cycles, representing an excellent stability of the electrode.

The influence of the scan rate on redox peaks at the BaD/PPy/PGE was investigated by CV. Fig. 5 shows the CV curves of BaD/PPy/PGE in 0.1 M NaAc-HAc solution (pH 5.0) with a scan rate ranging from 30 to 310 mV s$^{-1}$. It is evident that both the redox peak currents were enhanced by increasing the scan rate ($v$). As presented in inset 1 of Fig. 5, both the oxidation and reduction peak currents were linearly proportional to the scan rate. The regression equations were $I_{pa} = 11.3821 + 0.2220\, v$ ($\mu\text{A}$, mV s$^{-1}$, $R^2 = 0.9947$) and $I_{pc} = -6.4769 - 0.1301\, v$ ($\mu\text{A}$, mV s$^{-1}$, $R^2 = 0.9901$). The equations indicated that the redox reaction of the BaD/PPy/PGE electrode was a surface-controlled process.

Meanwhile, we also investigated the effect of scan rate on the peak potential and found that $E_{pa}$ shifted positively and $E_{pc}$ shifted negatively as the improving scan rate (Fig. 5 inset 2). The $E_{pa}$ and $E_{pc}$ were linearly dependent on the ln$v$ with the regression equations of $E_{pa} = -0.3710 + 0.01785\ln v$ (V, mV s$^{-1}$, $R^2 = 0.9871$) and $E_{pc} = -0.2881 - 0.01755\ln v$ (V, mV s$^{-1}$, $R^2 = 0.9844$). According to Laviron’s theory [33], the plot of $E_{p}$ vs ln$v$ yielded two straight lines with slopes of $-RT/\alpha nF$ and $RT/(1 - \alpha)nF$ for the reduction and oxidation peaks, respectively. The charge transfer coefficient, $\alpha$, was calculated to be 0.496 based on the slopes of the two straight lines of $E_{p}$ vs ln$v$ using the following equation:

$$k_a/k_c = \alpha/(1 - \alpha)$$

where $k_a$ and $k_c$ are the slope of the straight lines for $E_{pa}$ vs ln$v$ and $E_{pc}$ vs ln$v$, respectively. When $v$ was approximate to zero, both the oxidation and reduction peaks became close to reversible peaks with symmetrical shapes. The width of mid-height ($\sim 49\, \text{mV}$) became independent of $\alpha$ and moved toward 90.6/nA. Therefore, $n\alpha$ was calculated to be 2, indicating that two electrons were involved in the electrochemical redox process of BaD. The apparent heterogeneous electron transfer rate constant, $k_t = 4.46\, \text{s}^{-1}$, could also be obtained according to Laviron equation [33].

In addition, the effect of the pH value of solution on the peak current and potential were also investigated. Fig. 6 shows the influence of pH on the $I_{pa}$ and $E_{pa}$ at the BaD/PPy/PGE. When pH increases from 3.5 to 6.5, the $I_{pa}$ first gradually increases (3.5 to 5.0) and then

![Fig. 4](image-url) The CV curves of a) bare PGE, b) 0.5 mM BaD solution on the PPy/PGE and c) the BaD/PPy/PGE in pH 5.0 buffer solution.

![Fig. 5](image-url) CV curves of BaD/PPy/PGE in pH 5.0 buffer solution at scan rates 30 (a), 70 (b), 110 (c), 150 (d), 190 (e), 230 (f), 270 (g) and 310 (h) mV s$^{-1}$. Inset 1 is the linear relationship of the reduction/oxidation peak current ($I_p$) and the value of scan rate ($v$); Inset 2 is the linear relationship of the reduction/oxidation peak potential ($E_p$) and the logarithm value of scan rate (ln$v$).

![Fig. 6](image-url) The oxidation peak current and potential data of BaD/PPy/PGE with different pH (from 3.5 to 6.5).
declines (5.0 to 6.5). Therefore pH 5.0 solution was employed for the determination to maximize the sensitivity. Unlike $I_{pa}$, with the solution pH increasing, the $E_{pa}$ shifts negatively and linearly in the range of pH 3.5–6.5. The linear regression equation: $E_{pa} (V) = 0.0734 - 0.0696pH$, $R^2 = 0.9990$. According to the following formula [34]:

$$dE_{pa}/dpH = -2.303 \text{ mRT}/nF$$

(2)

The proton number ($m$) intervening in the oxidation process could be calculated as 2. Therefore, the possible electrode reaction mechanism of BaD/PPy/PGE was proposed in Scheme 2.

3.4. Influence of BkF on the electrochemical behaviors of BaD/PPy/PGE

Owing to the $\pi$-$\pi$ interaction between BaD and BkF, BaD/PPy/PGE can be applied in the detection of BkF. The DPV curves for PPy/BaD/PGE in 0.1 M NaAc–HAc buffer solution (pH 5.0) containing different concentrations of BkF were recorded. Due to the strong interaction between BkF and BaD, BkF could significantly affect the electrochemical response of BaD/PPy/PGE. Generally, both oxidation and reduction peaks of BaD/PPy/PGE decrease with the BkF concentration. Importantly, it was found that the oxidation peak current was more sensitive to the change of BkF concentration. Based on this phenomenon, the determination of BkF according to the oxidation peak current of BaD was established in this paper. Fig. 7 displays the relationship between the change of BaD oxidation peak current ($\Delta I_p$) and the logarithm of BkF concentration (lgc). In the range of $1.0 \times 10^{-12}$–$1.0 \times 10^{-9}$ M, $\Delta I_p$ changes linearly with the increasing of lgc, with a regression equation of $\Delta I_p = -45.45 - 3.678\text{lgc} (\mu A, M, R^2 = 0.9962)$ (Fig. 7, the inset). The detection limit is also evaluated to be as low as $1.0 \times 10^{-13}$ M for BkF. Importantly, the achieved detection limit is lower than published values based on chromatography and hyphenated techniques [35–38], ranging from $4.0 \times 10^{-12}$–$1.0 \times 10^{-9}$ M.

3.5. Influences of other PAHs on the $\Delta I_p$ of BaD/PPy/PGE

In order to investigate the selectivity of BaD/PPy/PGE, the influences of different aromatic ring PAHs on its electrochemical responses were analyzed (Fig. 8). The experiments show that BaA, BaP, NaP, BPE and p-chlorophenol have almost no effect on $\Delta I_p$ in the concentration range of $1.0 \times 10^{-12}$–$1.0 \times 10^{-9}$ M. However, PHE, ANT and PYR have a certain impact on $\Delta I_p$ in the same concentration range. These results indicate that the $\pi$-$\pi$ interaction between BkF and BaD is stronger than other PAHs and the BkF has a greater impact on the electrochemical properties of BaD, reflected by the reduction of the redox peaks current. Herein, the interference coefficient $S_{R,X}$ ($R$ represents BkF, $X$ represents other PAHs) was defined in order to characterize the selectivity:

$$S_{R,X} = C_R/C_X$$

(3)

where $S_{R,X}$ is the interference coefficient, $C_R$ and $C_X$ are the concentration of the BkF and other PAHs, respectively. When $\Delta I_p/I_p^0$ is decreased by 10%, with BkF concentration as the standard, the corresponding $S_{R,X}$ for each PAH are calculated in Table 1. The results demonstrated, again, that the interaction between BaD and BkF is the most significant among all the PAHs tested in this work.

3.6. Analytical application

In order to evaluate the applicability of the proposed method, the standard liquid sample containing 16 PAHs and the waste water samples of a coking plant were measured. A certain amount of standard liquid sample was added into 10.00 mL pH 5.0 NaAc–HAc buffer solution. The electrochemical responses of blank sample and standard solution were recorded by DPV and the obtained $\Delta I_p$ values were used to calculate the concentration of BkF based on linear equation: $\Delta I_p = -45.45 - 3.678\text{lgc}$. The results (Table 2) indicates that the BaD/PPy/PGE can be used to determine the concentration of BkF in the range of $1.0 \times 10^{-12}$–$1.0 \times 10^{-9}$ M.

In the meantime, the pH values of waste water samples of a coking plant were adjusted to 2.0 with 1:1 (v/v) HCl. Then, 1.0 mL of this sample was transferred to a 10 mL flask, adjusted pH values to 5.0 with 1.0 mol/L NaOH solution and diluted with 0.1 M NaAc–HAc (pH 5.0) to volume. Finally, a portion of as-prepared sample was transferred to the electrochemical cell. Using standard addition method, the recoveries of BkF were determined and the results were shown in Table 3. Noteworthy, the percentage recovery assays exhibited satisfactory recoveries of 99.2–106%, demonstrating that the

![Fig. 7. DPV curves for PPy-BaD/PGE in 0.1 M NaAc–HAc solution (pH 5.0). Inset is the calibration curve for BkF. a–h: 0, $1.0 \times 10^{-12}$, $5.0 \times 10^{-12}$, $1.0 \times 10^{-11}$, $5.0 \times 10^{-11}$, $1.0 \times 10^{-10}$, $5.0 \times 10^{-10}$, $1.0 \times 10^{-9}$ M.](image)

![Fig. 8. $\Delta I_p/I_p^0$ of BaD/PPy/PGE as functions of the concentrations of PAHs. a–i: BkF, BaA, BaP, BPE, PYR, ANT, NAP, p-chlorophenol.](image)

<table>
<thead>
<tr>
<th>PAHs</th>
<th>$c/M$</th>
<th>$S_{R,X}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BkF</td>
<td>$2.095 \times 10^{-12}$</td>
<td>-</td>
</tr>
<tr>
<td>BaA</td>
<td>$3.720 \times 10^{-11}$</td>
<td>0.05630</td>
</tr>
<tr>
<td>BaP</td>
<td>$2.748 \times 10^{-11}$</td>
<td>0.07623</td>
</tr>
<tr>
<td>PHE</td>
<td>$1.015 \times 10^{-11}$</td>
<td>0.2063</td>
</tr>
<tr>
<td>ANT</td>
<td>$6.941 \times 10^{-12}$</td>
<td>0.3018</td>
</tr>
<tr>
<td>PYR</td>
<td>$1.015 \times 10^{-11}$</td>
<td>0.2063</td>
</tr>
<tr>
<td>NAP</td>
<td>$4.357 \times 10^{-9}$</td>
<td>0.0004807</td>
</tr>
<tr>
<td>p-chlorophenol</td>
<td>$8.628 \times 10^{-9}$</td>
<td>0.0002428</td>
</tr>
<tr>
<td>BPE</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1: Selectivity coefficients.
proposed methods can be employed to monitor the PAHs pollutants in waste water. Therefore, the constructed electrochemical sensor based on Bd/Ppy electrode would be of great promise for use in the practical detection of BKF.

4. Conclusions

In this work, a novel Bd/Ppy/PGE for the electrochemical determination of BKF was fabricated using Bd as the probe for the detection of PAHs for the first time. The mechanism for the redox activity of Bd/Ppy/PGE was discussed, indicating that two electrons and two protons were involved in the electrochemical redox process of Bd. Based on this, the electrochemical behaviors of Bd/Ppy/PGE in the presence of BKF were investigated in details. Importantly, Bd/Ppy/PGE exhibited excellent stability, selectivity and sensitivity towards BKF with a detection limit as low as 1.0 × 10⁻¹³ M. In addition, the developed method was rapid, inexpensive and environmentally friendly. Therefore, the designed sensor would be of great significance in the practical detection of BKF in waste water.

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References


