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Electrochemical Oxidation and Voltammetric Determination of Basic Brown G at a Carbon Paste Electrode

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The electrochemical oxidation behavior and oxidation mechanism of Basic Brown G (BBG) were studied at a carbon paste electrode (CPE) for the first time. In pH 11.0 phosphate buffer, two irreversible oxidation peaks of BBG at 0.39 V and 0.78 V (versus SCE) were observed, which were both two-electron and two-proton process with diffusion character. The two peaks were assigned to the oxidation of 1, and 1'-phenylamine groups and the further oxidation of the oxidation products in the BBG molecule. The diffusion coefficient of BBG was assessed to be 8.7×10^{-5} cm^2 s^{-1}. A square wave voltammetric method was proposed for the determination of BBG. The peak current of the oxidation peak of BBG was linear with its concentration in the ranges from 0.004 to 0.2 μM and 0.2 to 2.0 μM, with a detection limit of 1.2 nM (3S/N). The proposed method was employed to the quantification of BBG in water samples.

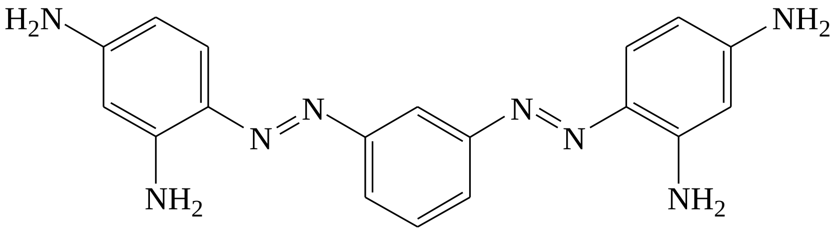
Keywords: Basic Brown G; Electrochemical Oxidation; Carbon Paste Electrode; Determination

1. INTRODUCTION

Basic Brown G (BBG, 4, 4'-[m-phenylenebis(azo)]-bis[m-phenylenediamine] dihydrochloride, structure shown in scheme 1) is an azo dye widely used in printing and dyeing textile industry [1]. It is released into the environment during the production and use, polluting the environment and causing great harm to organisms [2-5]. Hence, rapid and sensitive detection of these dyes is urgently needed. So far, several methods including liquid chromatography-atmospheric pressure ionization mass spectrometry, ion-pair liquid chromatography with photodiode array and electro-spray mass spectrometry detection, and capillary zone electrophoresis et al [6-10] have been reported for this purpose. But the expensive equipment or the tedious experimental procedures limit their wide application.

Voltammetry has been widely applied owing to its high sensitivity, rapid response, good selectivity, simplicity, and low-cost. Oliveira et al [11] reported the electrochemical sensing of hair dye basic brown 17 (BB17) on the self-organized Ti/TiO_2 nanotubular electrodes by monitor the reduction of BB17. Li et al [12] reported the determination of BBG and its interaction with cyclodextrins on the toxicity mercury electrode, based on the reduction of BBG by polarography and voltammetry. The peak current is proportional to the concentration of BBG over the range of 3.0×10^{-8} to 1.0×10^{-4} M with the limit of detection (LOD) of 9.0×10^{-9} M. They also reported the interaction of BBG with DNA and determination of DNA on a mercury electrode, based on the reduction of BBG [13]. BBG is also a derivative of phenylenediamine, which can be oxidized electrochemically [14-17]. However, the electrochemical oxidation of BBG has not been studied so far.

Besides, carbon paste electrode (CPE) has been broadly used as a working electrode owing to its advantages of a large potential window, low background current, simple preparation, easy renewal, and low cost [18-20]. Thus, in the present work, the electrochemical oxidation behavior and oxidation mechanism of BBG was studied at CPE by voltammetry for the first time. Furthermore, based on the voltammetric oxidation of BBG, a sensitive square wave voltammetric method for the quantification of BBG was developed.



Scheme 1. Structural formula of Basic Brown G

2. EXPERIMENTAL

2.1. Materials

Basic Brown G; graphite powder (spectral reagent), paraffin oil, potassium hexacyanoferrate ($K_3[Fe(CN)_6]$), phosphoric acid (H_3PO_4, 85%), sodium hydroxide (NaOH), sodium dihydrogen phosphate (NaH_2PO_4), acetic acid (HAc), sodium acetate (NaAc), aqueous ammonia ($NH_3\cdot H_2O$), ammonium chloride (NH_4Cl), ammonium sulphate [$(NH_4)_2SO_4$], ammonium nitrate (NH_4NO_3), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), manganese sulfate ($MnSO_4$), cadmium sulfate ($CdSO_4$), ethylenediamine, absolute ethanol, fructose, and glucose were purchased from Aladdin Chemical Reagents Co., Ltd.. All the chemicals used were of analytical-pure grade. Twice-distilled water was used throughout the experiments.

2.2. Apparatus

Electrochemical measurements were carried out on a CHI 650C electrochemical workstation (Chenhua Instrument, Shanghai, China). A conventional three-electrode system including a homemade

CPE working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter electrode was employed. And the pH value of a solution was measured by a PB-10 Precision pH Meter (Sartorius, Germany). All the potentials quoted in the present work were referred to SCE. All experiments were carried out at room temperature.

2.3. Electrode preparation and activation

CPE was prepared by mixing graphite powder and paraffin oil in a ratio of 5:2 (w/w) in an agate mortar [21]. A portion of the resulting paste was packed firmly into the cavity (3.0 mm diameter) of a Teflon tube. The electric contact was established via a copper wire. The surface of the electrode was smoothed on a tracing paper and rinsed with water. The CPE was activated by CV scanning in the potential range of 0 ~ 1.0 V at 100 mV s^{-1} in pH 11.0 PBS solution for 20 cycles until a stable background current was obtained.

2.4. Experimental procedure

A 10 mL volume of 0.1 M PBS (pH 11.0) solution containing an appropriate BBG was transferred into a voltammetric cell. The cyclic voltammograms were recorded between the potential range of 0.0 ~1.0 V at the scan rate of 100 mV s^{-1}. After each measurement, the CPE was refreshed by washing with water and then by CV scanning from 0.0 ~ 1.0 V by 10 cycles in 0.1 M PBS (pH 11.0) solution until the voltammograms became stable. If necessary, the surface was renewed by pushing a thickness of 2~3 mm carbon paste out of the tube, followed by polishing on the tracing paper and washing with water.

2.5. Water sample analysis

The water samples were pre-treated by a simple filter to remove insoluble impurity. Then, microliters of the water samples were added into 10 mL pH 11.0 PBS solution. The square wave voltammograms were recorded between 0.1 and 1.1 V. The oxidation peak current of BBG was measured. The parameters of square wave voltammetry (SWV) were increment potential of 6 mV, pulse amplitude of 50 mV, and frequency of 50 Hz. The concentration of BBG was calculated using the standard addition method.

3. RESULTS AND DISCUSSION

3.1. Electrochemical oxidation behavior of BBG

The cyclic voltammograms of BBG at the CPE in the potential range of 0.0 to 1.0 V were shown in Fig. 1. In 0.1 M PBS solution (pH 11.0) containing 1.0×10^{-5} M BBG, BBG shows two oxidation peaks, the peak P_{a1} and the peak P_{a2} on the first anodic scan (Fig. 1, curve a). The peak P_{a1} appears at 0.39 V and the peak P_{a2} at 0.78 V, respectively. On the reversal scan, no corresponding reduction peaks were detected, indicates that the oxidation process of BBG is irreversible. Meanwhile, the oxidation peak currents show a large decrease on the second cyclic scanning; after the second scan, the peak P_{a2} disappears completely, the peak current of P_{a1} decreases slightly and finally reaches a constant level, indicating the adsorption of BBG oxidation products on the CPE surface. Moreover, after successive CV scan recorded, the CPE was washed with DI water and then transferred to the same supporting electrolyte solution containing 1.0×10^{-5} M BBG, the very same CV voltammograms as Fig.1 was obtained, indicating that the weak adsorption of BBG oxidation products can be easily washed by water.

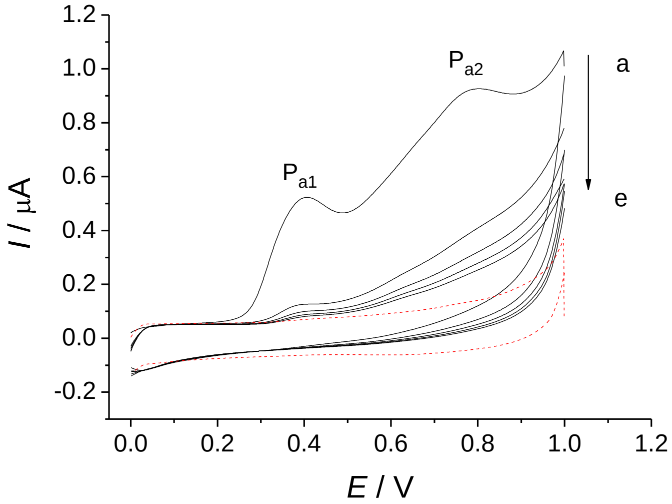


Figure 1. Cyclic voltammograms of BBG in 0.1 M PBS solution (pH 11.0) at CPE in the absence (dashed line) and the presence (solid line) of 1.0×10^{-5} M BBG. Scan cycles: a–e from the outer to the inner. Scan rate: 100 mV s^{-1}.

It is reported that phenylenediamine can be oxidized and electrochemical polymerized in acid and neutral condition, but can not form polymers in alkaline condition [22]. So, the oxidation peak P_{a1} and peak P_{a2} can be assigned to the electrooxidation of phenylenediamine group in the BBG molecule and the further oxidation of the oxidation product of P_{a1}, respectively [23, 24].

3.2. Electrochemical oxidation mechanism of BBG

To further study the electrochemical oxidation mechanism of BBG, the effect of scan rate *v* and the solution pH value to the oxidation of BBG were studied.

3.2.1. Effect of scan rate v to the oxidation peaks of BBG

The effect of scan rate *v* on the peak P_{a1} and the peak P_{a2} were examined (shown in Fig. 2). The peak currents I_{pa1} of the peak P_{a1} and I_{pa2} of the peak P_{a2} increase linearly with the square root of the scan rate *v* from 40 to 200 mV s^{-1}, the linear regression equation are I_{pa1} (μA) = $-0.123 + 0.0571\ v^{1/2}$ (mV $s^{-1})^{1/2}$ (r = 0.996, n = 6) for the peak P_{a1}, and I_{pa2} (μA) = $-0.361 + 0.112\ v^{1/2}$ (mV $s^{-1})^{1/2}$ (r =

0.992, n = 6) for the peak P_{a2}, respectively, which are consistent with the diffusion-controlled oxidation process [25, 26].

For a diffusion-controlled irreversible system, the relationship between the I_{pa} and $v^{1/2}$ is given by the Randles-Sevcik equation [27, 28],

$$I_{pa} = 2.99\times10^5 n(\alpha_c + n')^{1/2} A C_o D_o^{1/2} v^{1/2} \quad \text{(Eq. 1)}$$

According to the slop of the plot of I_{pa1} vs. $v^{1/2}$ (Fig. 2B), the diffusion coefficient of BBG is estimated to be 8.7×10^{-5} cm^2 s^{-1}.

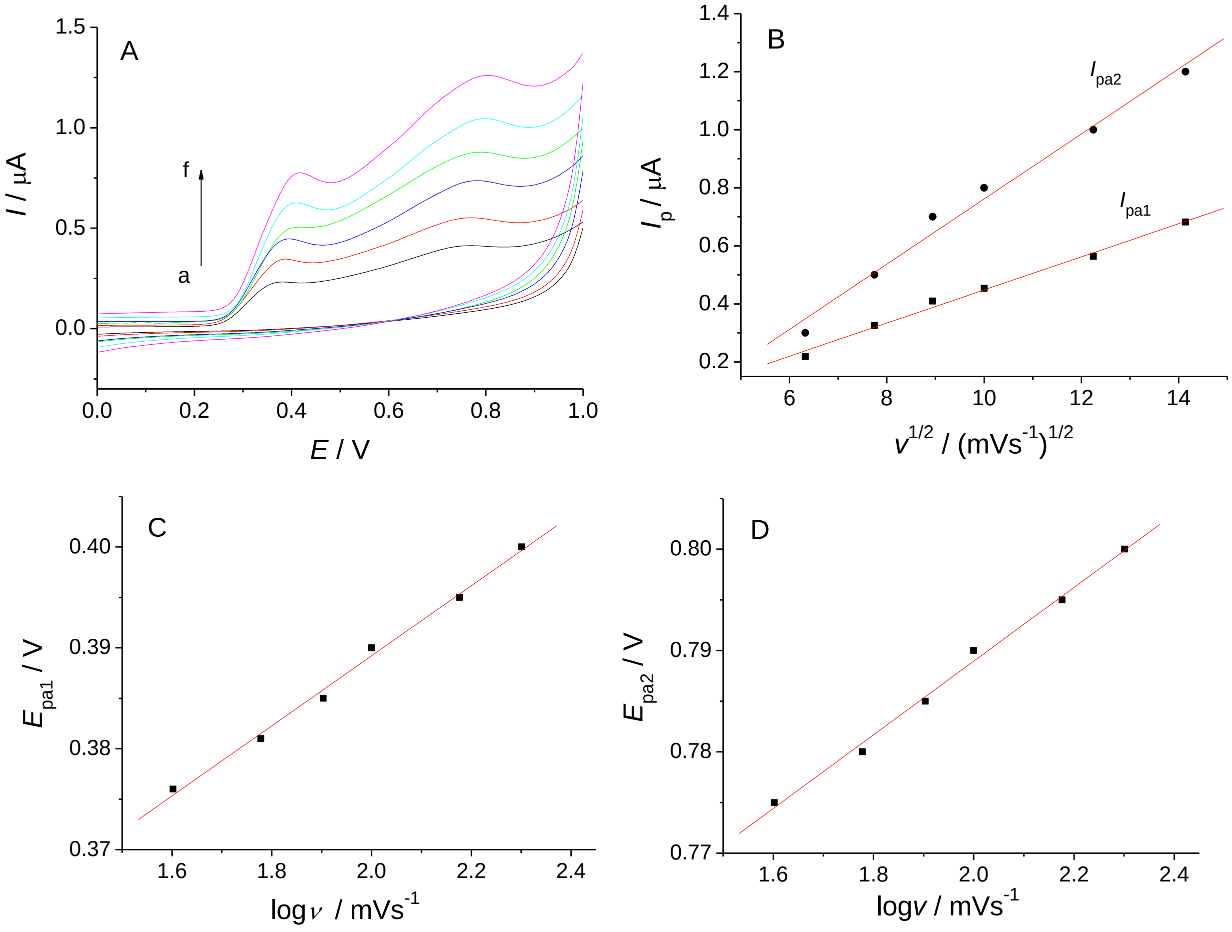


Figure 2. (A) Cyclic voltammograms of 1.0×10^{-5} M BBG in 0.1 M PBS solution (pH 11.0) at scan rate of (from a to f): 40, 60, 80, 100, 150, 200 mV s^{-1}. (B) Plots of I_p vs. $v^{1/2}$. (C) Plot of E_{pa1} vs. log$v$. (D) Plot of E_{pa2} vs. log$v$.

In this case, the difference between peak potential E_{pa1} and the potential at half height of peak $E_{pa1/2}$ was determined to be 45 mV. According to $|E_{pa1}-E_{pa1/2}| = 47.7/(\alpha_c + n')$ for a diffusion-controlled irreversible system, $(\alpha_c + n')$ was calculated to be 1.06. Meanwhile, the CPE electroactive area A was determined by the Randles-Sevcik equation for a reversible system, $I_{pa} = 2.69\times10^5 n^{3/2} A C_o D_o^{1/2} v^{1/2}$. Based on the slope of I_{pa} vs. $v^{1/2}$ (Fig. 3), the concentration of hexacyanoferrate solution (1 mM), and the value of the diffusion coefficient of hexacyanoferrate in phosphate buffer (D_o= 7.6×10^{-6} cm^2 s^{-1}) [29, 30], the electroactive area A of the CPE was estimated to be 0.033 cm^2.

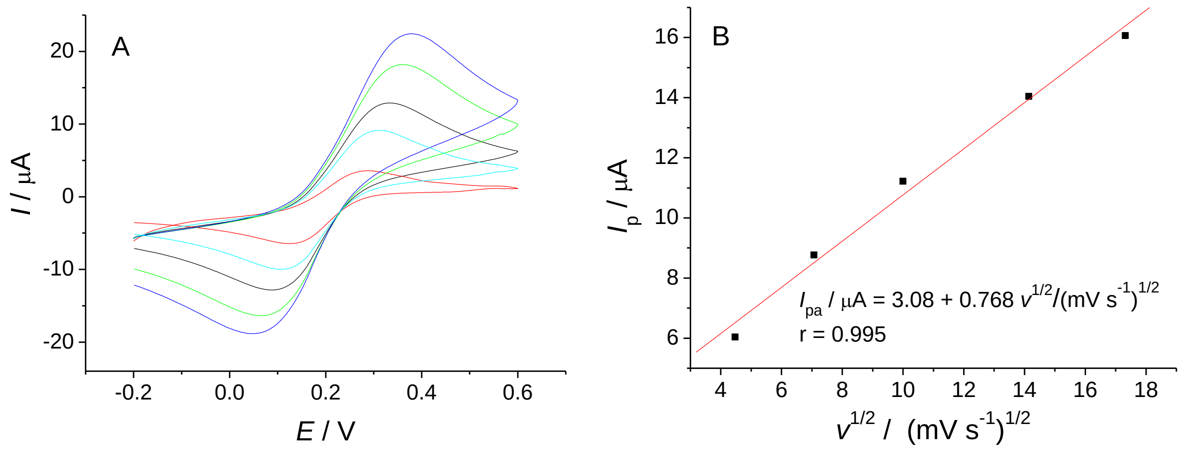


Figure 3. (A) Cyclic voltammograms of CPE in 0.1 M KCl solution containing 1 mM $[Fe(CN)_6]^{3-/4-}$ at different scan rates (from inner to outer): 20, 50, 100, 150, 200, 250, 300 mV s^{-1}. (B) Plot of I_{pa} vs. $v^{1/2}$.

Furthermore, the peak potential E_{pa1} of the peak P_{a1} and E_{pa2} of the peak P_{a2} shift gradually to the positive direction. The plots of the peak potential E_{pa1} and E_{pa2} versus the logarithm of the scan rate v follow the linear regression equation of E_{pa1} (V) = 0.319 + 0.035 log v (mV s^{-1}) (r = 0.997, n = 6), and E_{pa2} (V) = 0.716 + 0.036 log v (mV s^{-1}) (r = 0.997, n = 6), respectively. For a diffusion-controlled irreversible process, the relationship of the peak potential E_p with the logarithm of the scan rate v obeys the following equation [31]:

$$E_{pa} = E^{o'} + \frac{RT}{(1-\alpha)nF}\left\{0.780 + \ln\left(\frac{D_R^{1/2}}{\kappa^{o}}\right) + \ln\left[\frac{(1-\alpha)nFv}{\kappa T}\right]^{1/2}\right\} \quad \text{(Eq. 2)}$$

where the coefficient α of electrons transferred is assumed to be 0.5. From the slope of 0.035 for the plot of E_{pa1} vs. log$v$, and 0.036 for the plot of E_{pa2} vs. log$v$, the number n of electrons transferred are calculated to be 1.7 (approximately 2) for P_{a1}, and 1.6 (also approximately 2) for P_{a2}, respectively.

3.2.2. Effect of pH value to the oxidation peaks of BBG

Several supporting electrolytes such as HAc-NaAc, Britton-Robinson, $NH_3{\cdot}H_2O$-NH_4Cl, and phosphate buffer solutions were tested. The results show that the peak P_{a1} and P_{a2} of BBG oxidation are more stable and sensitive in phosphate buffer solution (PBS) than those in other supporting electrolytes. Since the peak P_{a2} could not be detected when pH value was below 8 in the present potential windows, the effect of pH on the peak P_{a1} and P_{a2} were examined in the pH ranges of 4.0 to 12.0 and 8.0 to 12.0, respectively. As shown in Fig. 4, the peak currents I_{pa1} and I_{pa2} increase gradually with the increase of pH values and achieve the maximum value at pH 11.0. When pH was above 11.0, the peak currents decrease gradually. Thus, 0.1 M PBS solution (pH 11.0) is selected as supporting electrolyte. At the same time, the peak potential E_{pa1} of the peak P_{a1}, and E_{pa2} of the peak P_{a2} shift negatively, and obey the following linear regression equation of E_{pa1} (V) = 0.861 – 0.048 pH (r =

0.988, n = 9), and E_{pa2} (V) = 1.425 – 0.062 pH (r = 0.993, n = 5), respectively. From the slopes of the E_p vs. pH relationship, the numbers of protons taking part in the peak P_{a1} and the peak P_{a2} electrode reaction processes are equal to those of electrons.

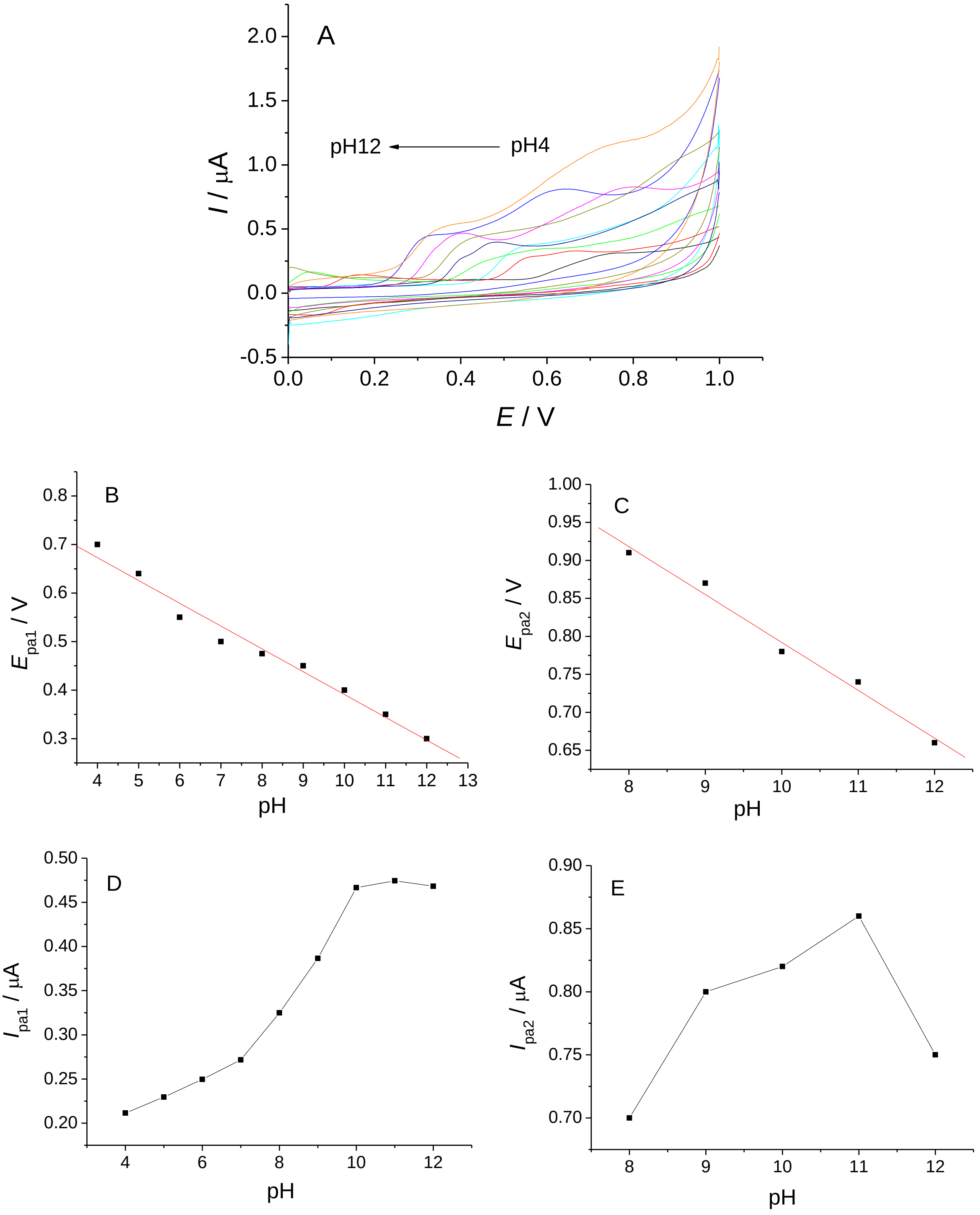
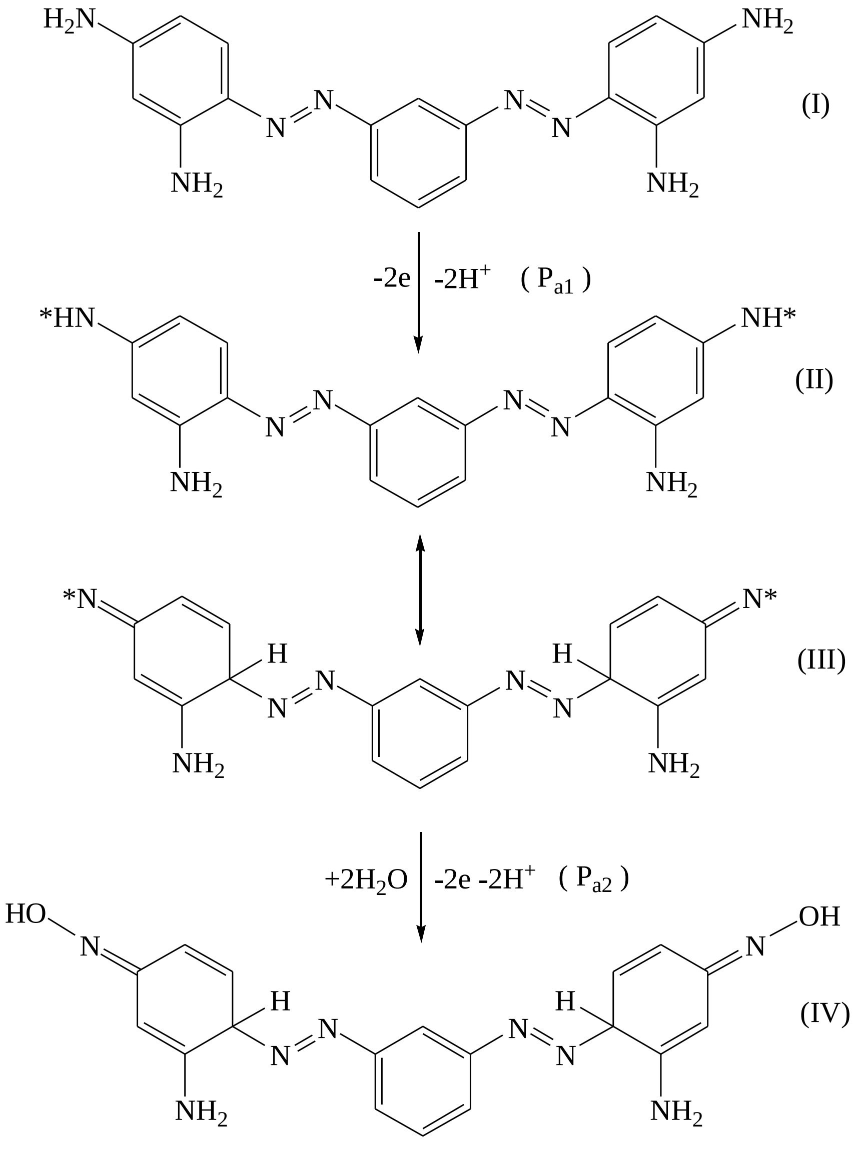


Figure 4. (A) Cyclic voltammograms of 1.0×10^{-5} M BBG in 0.1 M PBS solution (pH 11.0) with various pH values. Scan rate: 100 mV s^{-1}. (B) Plot of E_{pa1} vs. pH. (C) Plot of E_{pa2} vs. pH. (D) Plot of I_{pa1} vs. pH. (E) Plot of I_{pa2} vs. pH.

Based on the above analysis, the peak P_{a1} can be assigned to the oxidation of 1, and 1'-phenylamine groups I to the phenylamino radicals II by a two-electron transfer and two-proton dissociation process, then, the phenylamino radicals change to phenylimino radicals III through isomerization, and the further oxidation of the phenylimino radicals to the phenyloxime groups IV produces the peak P_{a2} [32]. The steric hindrance effect makes the electrochemical oxidation of 1, and 1'-phenylamine groups are more favored than the 3, and 3'-ones. Therefore, the electrochemical oxidation mechanism of BBG is presented in Scheme 2.



Scheme 2. Electrochemical oxidation mechanism of Basic Brown G

3.3. Voltammetric determination of BBG

Based on the oxidation peak current of BBG, a voltammetric method for the determination of BBG is proposed. As the peak P_{a2} of BBG oxidation is more sensitive than the peak P_{a1}, the peak P_{a2} is chosen for the quantitative analysis. Meanwhile, square wave voltammetry is used to record the voltammogram due to its high sensitivity and excellent resolving power.

3.3.1. Calibration curve

The square wave voltammograms (SWV) of BBG at CPE in 0.1 M PBS solution (pH 11.0) were shown in Fig. 5. As shown, the response currents increase with the increase of BBG concentration, and are linear with BBG concentration in the range of 0.004 to 2 μM. Two linear ranges were observed. The linear regression equations are I (μA) = 0.062 + 1.333c (μM) (c = 0.004 ~ 0.2 μM, r = 0.996), and I (μA) = 0.217 + 0.505c (μM) (c = 0.2 ~ 2 μM, r = 0.997), respectively. The detection limit is 1.2 nM (3S/N), which is lower than the literature reported 9.0 nM [12].

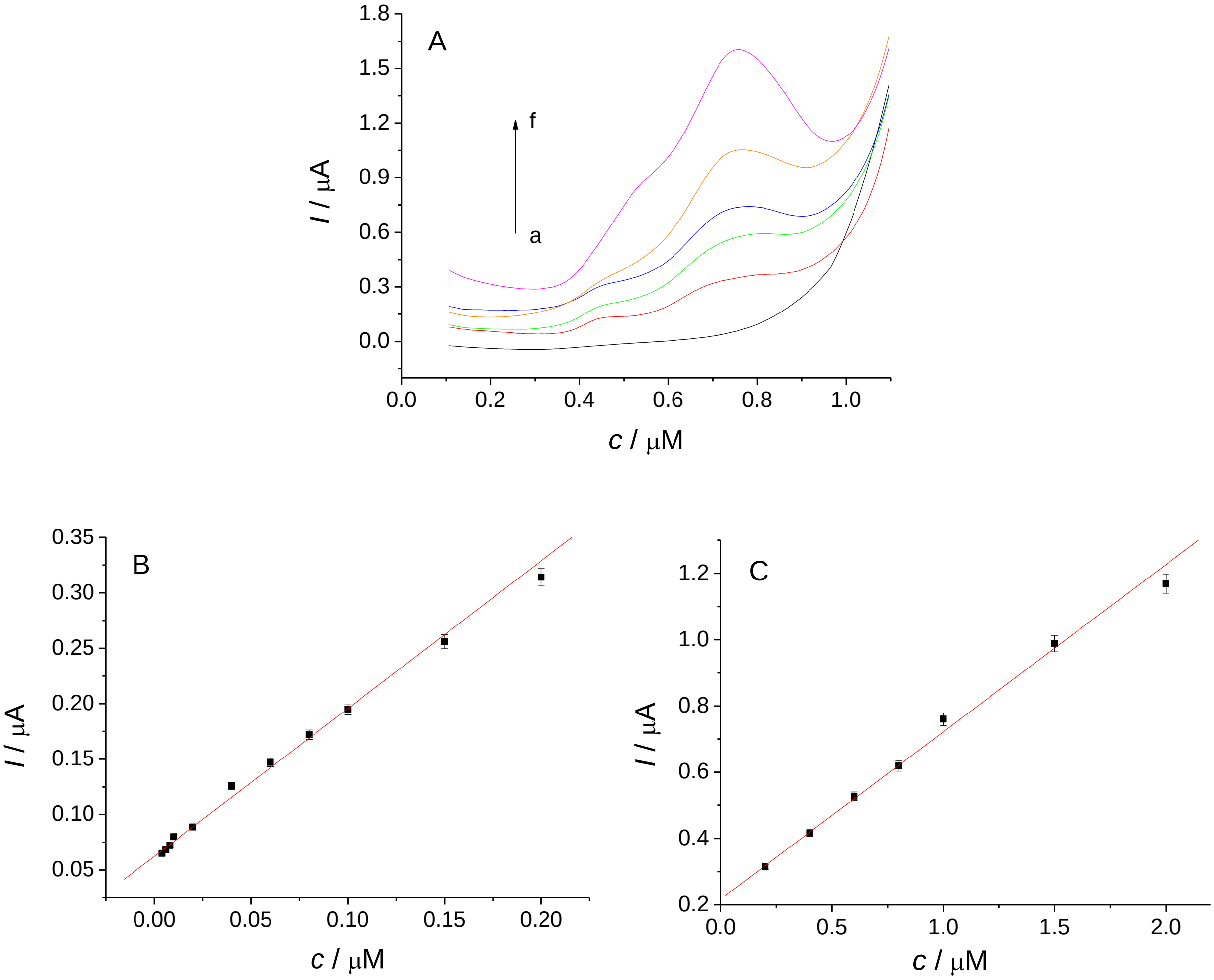


Figure 5. (A) Square wave voltammograms of BBG in 0.1 M PBS solution (pH 11.0). The concentration of BBG for a to f are: 0, 0.004, 0.04, 0.1, 0.4, 1.0 μM. (B) Plot of I_{pa} vs. BBG concentration from 0.004 to 0.2 μM. (C) Plot of I_{pa} vs. BBG concentration from 0.2 to 2.0 μM.

3.3.2. Repeatability, reproducibility, and interferences

The repeatability and reproducibility of the proposed method were studied. The relative standard deviation (RSD) for seven replicate measurements of 0.5 μM BBG at CPE is 2.12 %. The

RSD of six pieces of CPE with the same surface area for the individual quantification of 0.5 μM BBG is 2.85 %, demonstrate the good repeatability and reproducibility of the proposed method.

The influence of some interferences on the quantification of BBG was also tested. The tolerable limit is defined as the concentration of possible interfering species, which gives a relative error of less than ± 5.0 % in the quantification of 0.5 μM BBG. The results show that 500-fold of NH_4^+, Cl^-, Ac^-, NO_3^-, SO_4^{2-}, and ethylenediamine, 200-fold of Ca^{2+}, Mg^{2+}, Mn^{2+}, Cd^{2+}, ethanol, fructose, and glucose do not interfere with the quantification, proving the good selectivity of the proposed method.

3.3.3. Quantification of BBG in water samples

The potential application of the proposed method was evaluated by monitoring the concentration of BBG in water samples. Standard addition method was used for the analysis. As seen in Table 1, the recoveries are in the range of 95.6 % to 101 %, suggesting that the proposed method is promising for detecting BBG in the real samples.

Table 1. Results of quantification of BBG in water samples

Sample	BBG added (μM)	BBG found (μM)*	Recovery (%)
waste water	0	–	–
	0.0100	0.00968	96.8
	0.100	0.101	101
	0.800	0.777	97.1
river water	0	–	–
	0.0100	0.00989	98.9
	0.100	0.0956	95.6
	0.800	0.795	99.4

* Mean value of five measurements.

4. CONCLUSIONS

The electrochemical oxidation behavior and oxidation mechanism of BBG were investigated for the first time at a carbon paste electrode. The oxidation of BBG was found to be diffusion-controlled irreversible processes. The two oxidation peaks can be assigned to the oxidation of 1, and 1'-phenylamine groups to the phenylamino radicals, and the further oxidation of the phenylamino radicals to the phenyloxime groups. The diffusion coefficient of BBG (D_{BBG}) was calculated to be 8.7×10^{-5} cm^2 s^{-1}. A square wave voltammetric method for the quantification of BBG was proposed. The proposed method possesses the property of simplicity, rapidity and high sensitivity.

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