

# Electrochemical deposition and mechanism investigation of Prussian blue on graphic carbon paste electrode from an acidic ferricyanide solution

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**Abstract** Prussian blue (PB) films were electrochemically deposited on graphite carbon paste electrodes (GCPEs) from an acidic solution of ferricyanide using the potentiodynamic and potentiostatic techniques. Interestingly, we, for the first time, observed that on the surface of GCPE, the electrochemistry of PB films strongly depended on the deposition potential. A maximum formation rate of PB was obtained at a more positive deposition potential (0.4 V vs saturated calomel electrode) on GCPE than that on Au or Pt electrode. The ratio of peak current at ca 0.75 V to the one at 0.19 V varied with the deposition potential. In addition, the electrocatalytic activity of the modified GCPEs towards the reduction of hydrogen peroxide considerably changed with the formation potentials of the PB films. These phenomena can be due to the different formation mechanism of PB at different deposition potentials.

**Keywords** Prussian blue · Ferricyanide · Electrodeposition · Mechanism · Surface chemistry

## Introduction

Chemically modified electrodes have attracted considerable interests over the past two decades, as researchers have been attempting to exert more direct control over the chemical nature of electrodes. Among various materials used for the

electrode modification, transition metal hexacyanoferrates have been widely studied as excellent electron transfer mediators [1–6]. Recently, Prussian blue (PB) and its analogues-modified electrodes have been used for the detection of various analytes, including hydrogen peroxide [7–9], ascorbic acid [10–12], glucose [13–15], and other compounds [16–18].

In our previous studies, we successfully deposited PB films on gold and polycrystalline Pt disk electrodes by the electrochemical method from an acidic solution containing single component of ferricyanide, and the deposition mechanism was proposed as well [19, 20]. By using this electrochemical deposition method, PB clusters were successfully loaded on the Au and Pt electrode surfaces. The maximal formation rate of PB occurred at a relatively negative potential (e.g., –0.5 and –0.42 V vs SCE for Au and Pt electrodes, respectively) due to the strong specific adsorption of  $\text{CN}^-$  ion on the surface of noble metallic electrodes over a wide potential range [19, 20]. The strong adsorption of  $\text{CN}^-$  ions decreases the active site on the electrode surface for the reduction of ferricyanide ions and dissociated ferric ions and subsequently inhibits the electrochemical deposition of PB clusters. Therefore, it would be interesting to know the formation of PB on electrodes with weak affinities towards the  $\text{CN}^-$  ion adsorption.

Graphite carbon paste electrodes (GCPEs) have been widely used for the construction of biosensors because of their easy preparation, modification [21–24], and low background current in electrochemical analysis [25, 26]. In addition, the electrode surface can be easily renewed. Up to now, many methods have been reported for the fabrication of PB-modified GCPEs, including (1) the direct mixing technique: mixing PB nanocrystals with graphite powder to fabricate carbon paste electrodes [27–30], which represents a simple and effective way to add inorganic,

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Dedicated to Prof. Dr. Teresa Iwasita on the occasion of her 65th birthday in recognition of her numerous contributions to interfacial electrochemistry.

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organic, or biological modifiers to the electrode material; (2) in situ PB formation method: preparing PB in the graphite carbon powder solution, which allows the chemical deposition of PB clusters onto graphite by a simple chemical reaction [31]; (3) surface immobilization approach: immobilizing metal hexacyanoferrates on the surface of GCPE mechanically [32, 33]; (4) electrochemical deposition method: immersing a GCPE in a solution containing hexacyanoferrates and transition metal ions, which allows the formation of insoluble metal hexacyanoferrates by cycling the electrode within a suitable potential window [34, 35] or maintaining the electrode at a special potential in a period of time [19, 20].

In this paper, to investigate the electrochemical properties of PB modified GCPEs, an electrochemical deposition method from an acidic solution containing single component of ferricyanide was employed in comparison with our previous studies on Au and Pt electrodes. PB films were successfully formed on the surface of GCPEs using both the potentiodynamic and potentiostatic techniques. The influence of deposition potential on the formation rate and mechanism of PB films was studied. The electrochemistry of the PB–GCPEs formed at different potentials in blank electrolyte of potassium sulfate and in phosphate buffered solution (PBS) with and without the addition of hydrogen peroxide was also investigated.

## Materials and methods

**Chemicals** Ferricyanide and other chemicals were of analytical reagent grade and used as received. Solutions were prepared with deionized water from a pure system ( $>18.2 \text{ M}\Omega$ , PureLab Classic, USA).

**Instrumentation** Electrochemical measurements were performed with a CHI830 electrochemical workstation (CH Instrument, USA) in a traditional three-electrode electrochemical cell. Either GCPE or PB-modified GCPE was used as the working electrode; a saturated calomel electrode (SCE) and a platinum sheet were used as the reference and counter electrodes, respectively.

**Methods** Graphitic carbon paste electrodes were prepared by pressing the mixture of graphite powder and paraffin oil (65:35 w/w) in a glass tube (inner diameter of 350–400  $\mu\text{m}$ ). A copper wire providing an external electrical contact was inserted into the carbon paste from the backside and stuck reversibly on the exterior face of glass capillary using adhesive tape. By pushing the copper wire forward, the GCPE surface can be easily renewed by polishing it on a weighing paper. Then, PB was deposited on the polished GCPEs by scanning in the potential range from  $-0.2$  to

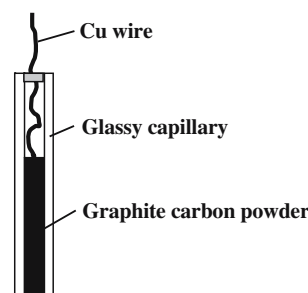
$+0.9 \text{ V}$  (at a scan rate of 100 mV/s) or by the potentiostatic method at a specified potential in a fresh solution containing  $1 \times 10^{-3} \text{ M K}_3\text{Fe}(\text{CN})_6 + 0.1 \text{ M K}_2\text{SO}_4$ . For making a meaningful comparison with our previous results on Au and Pt electrodes, the pH value of the electrolyte was adjusted to 1.6 using HCl solution. At this pH value, more  $\text{Fe}^{3+}$  ions were produced via the dissociation of ferricyanide, and more PB could thus be formed using the electrochemical method [19, 20]. After deposition, the PB modified GCPEs were taken out and rinsed thoroughly in water.

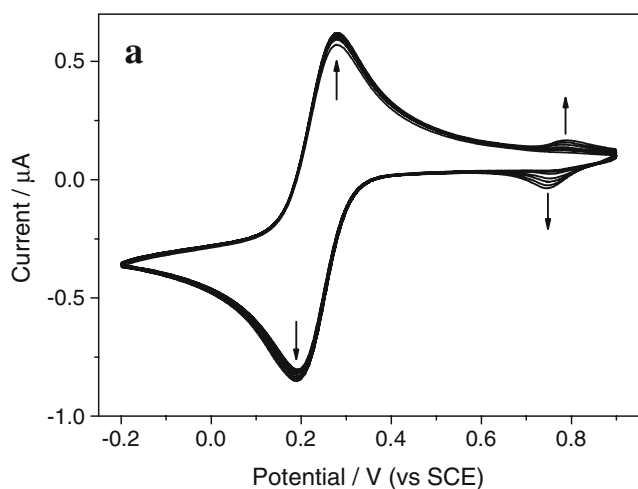
## Results and discussion

### Potentiodynamic deposition of PB on GCPE

Figure 1 shows the illustration of a GCPE in a glass capillary. Deposition of PB was carried out by cyclic potential sweep of a GCPE between  $-0.2$  and  $0.9 \text{ V}$  vs SCE in an acidic solution of  $1.0 \times 10^{-3} \text{ M K}_3\text{Fe}(\text{CN})_6 + 0.1 \text{ M K}_2\text{SO}_4$  (pH 1.6) at a scan rate of 100 mV/s. The cyclic voltammograms (CVs) of the GCPE in the deposition electrolyte showed two pairs of redox couple (Fig. 2a). One pair of redox couple is located at 0.19/0.24 V for the cathodic and anodic peak, respectively. This pair of peaks was mainly due to the electrochemical oxidation and reduction of  $\text{Fe}(\text{CN})_6^{3-/4-}$ . With the potential sweep going, the peak currents increased slowly due to the gradual formation of PB. The linear increase in current with the square root of scan rate indicated that the corresponding reaction was diffusion limited (not shown in the paper) [36]. Another new couple of peaks appeared at more positive potentials (the cathodic peak at 0.75 V vs SCE), which can be due to the redox reaction of PB/Berlin green (BG). An obvious increase in peak current occurred as the potential scanning time increased, which confirmed the increased amount of PB on the electrode surface. Comparing these two couple of peaks, it can be seen that the peak at ca 0.75 V (Fig. 2b, curve b) increased much faster than that of the one at ca 0.19 V (Fig. 2b, curve a). This faster increase rate can be due to the different PB formation mechanism.

**Fig. 1** Cross-sectional illustration of a graphite carbon paste electrode

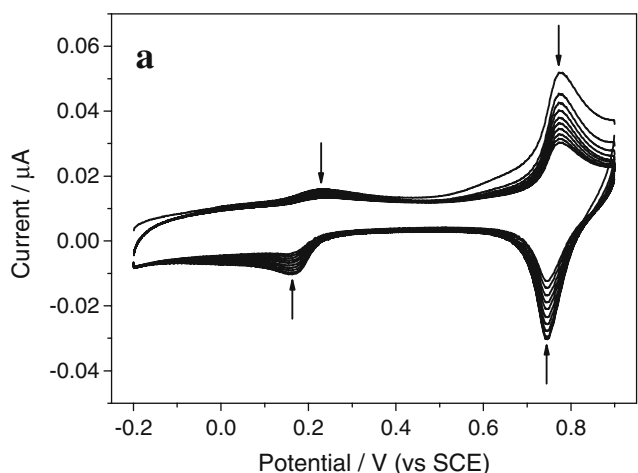
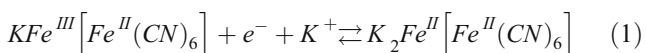




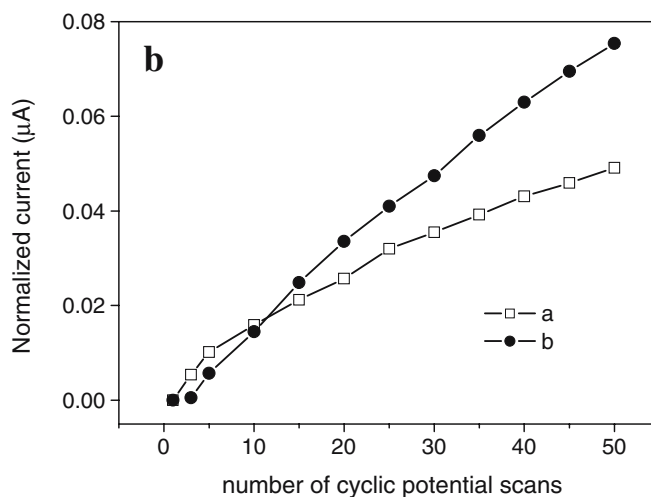
**Fig. 2 a** CVs of a GCPE in an acidic solution of  $1.0 \times 10^{-3}$  M  $K_3Fe(CN)_6 + 0.1$  M  $K_2SO_4$  (pH 1.6) for the first, third, fifth, tenth, 20th, 30th, 40th, and 50th potential scans with a scan rate

Electrochemical behavior of the prepared PB film on GCPE

The peak currents for the two pairs of peaks at 0.19 and 0.75 V kept almost constant after the 50th potential scan in the deposition electrolyte (Fig. 2a), indicating that a saturation PB layer was formed on the electrode surface. The electrochemistry of the modified electrode was investigated in a blank solution of 0.1 M  $K_2SO_4$  at 50 mV/s. CVs in the potential window between -0.2 and 0.9 V displayed the typical redox characteristics of PB modified electrodes. The pair of peaks located at around 0.19 V (Ox/Red-1) corresponds to the electrochemical transform between PB and Prussian white (PW; Eq. 1) [37]:

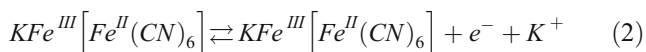


**Fig. 3 a** The first ten CVs of a PB-film-modified GCPE in a solution of 0.1 M  $K_2SO_4$  at a scan rate of 50 mV/s and **b** plots of the cathodic currents of peaks at 0.19 V (curve a) and 0.75 V (curve b) vs the sweep number corresponding to **a** (current for the first cycle was set to 0)

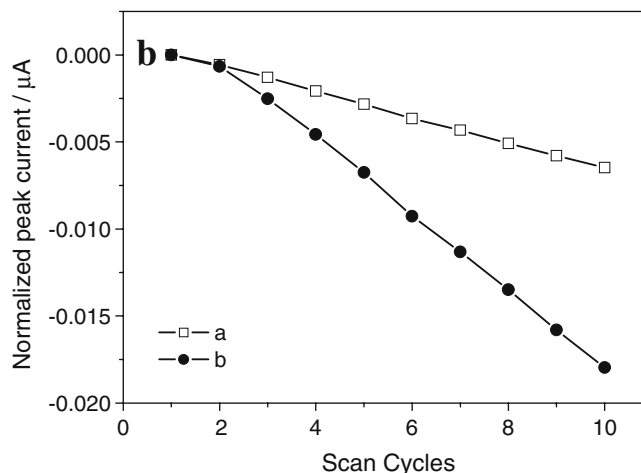


of 100 mV/s and **b** plots of the normalized cathodic peak current at 0.19 V (a) and 0.75 V (b) vs the cyclic number of potential scans (the current for cycle 1 was set to 0)

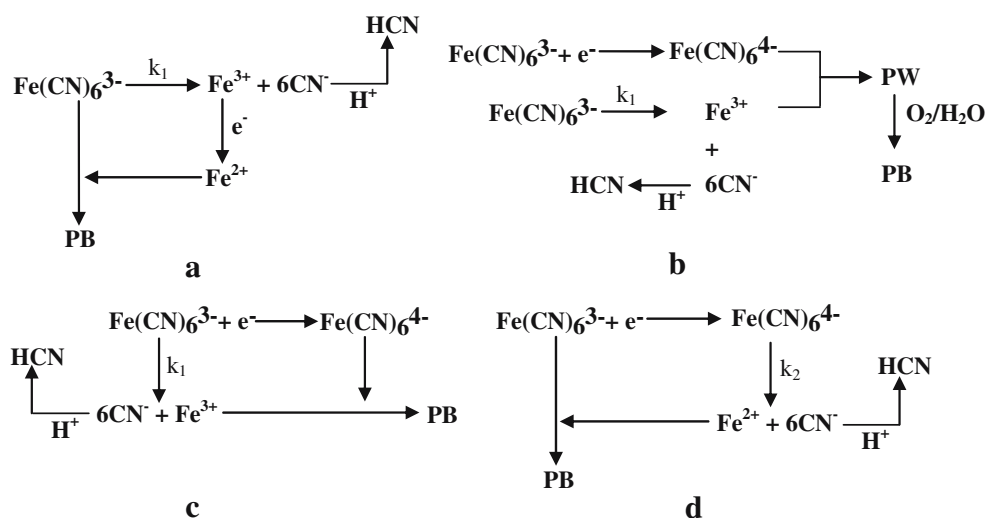
while the pair of peaks centered at ca 0.75 V (Ox/Red-2) refers to the transform between PB and BG (Eq. 2) [37]:



However, the relative current intensity of these two pairs of redox peaks and the stability of the PB film on GCPE were totally different from the previous reports on gold or platinum electrode [19, 20]. On one hand, the reduction peak of PB to Everitt's salt in the first CV was broad, with a half-width of ~130 mV and a peak separation of ~85 mV (Fig. 3a) which was much broader than the previous report value (~15 and 10 mV, respectively) on the platinum or gold substrate [38], while the oxidation peak for the oxidation of PB to BG (with a half-width of ~65 mV) was narrower than that of PB thin film on the noble metal electrode (~130 mV) [38]. On the other hand, the peak current and the integral



**Fig. 4** Four possible routes for the formation of PB on a GCPE in an acidic solution of single ferriicyanide



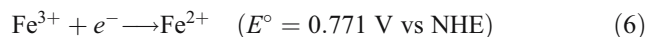
area of Ox/Red-2 were threefold and 2.2-fold larger than those of Ox/Red-1, respectively (Fig. 3a). This is totally different from the results on Au or Pt substrate. It was reported that around one third of the ferrocyanide ions in the PB at an Au or Pt electrode remained unoxidized [38]. The possible reason for this different phenomenon could be attributed to the difference in the formation mechanism of PB films on the GCPE and Au/Pt electrodes.

When the potential window was limited in the range of  $-0.2$  to  $0.6$  V, the CV of PB–GCPE in a solution of  $0.1$  M  $K_2SO_4$  is stable within 100 potential sweeps (not shown here). This implied that the PB film was relatively stable for the transition between PB and PW, e.g., intercalation of potassium cations in or out of the PB film would not damage the zeolitic structure. However, when the upper potential was extended to  $0.9$  V, both the Ox/Red-1 and Ox/Red-2 peaks diminished with the potential scanning time. When the upper limit potential was extended to the electrochemical oxidation of PB to BG, the zeolitic structure of PB would be destroyed gradually, which resulted in the decrease in peak currents.

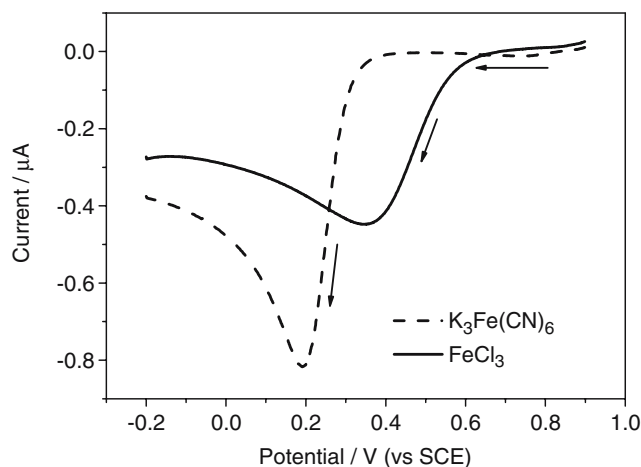
#### The formation mechanism of PB

According to our previous report [19], the source for providing free metallic ions can only be the dissociation of ferriicyanide. The main driving forces of this dissociation are provided by the evolution of HCN and the formation of PB in acidic solution. Thus, the following four possible routes for the formation of PB on GCPE can occur [Fig. 4, (a)–(d)]:

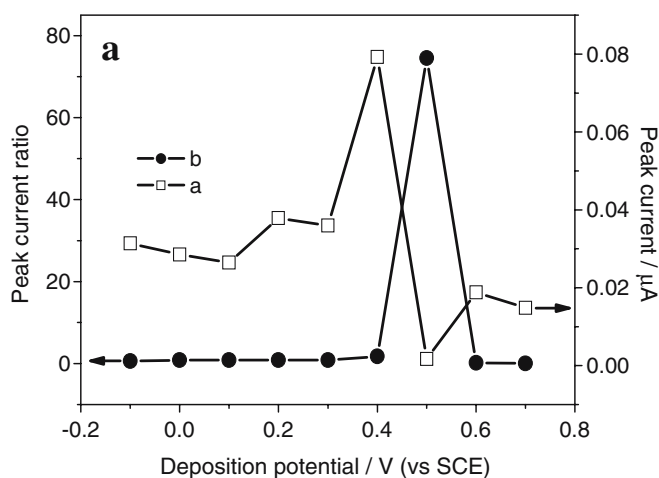
Figure 4 displays two dissociation processes and two electrochemical reactions as described in Eqs. 3, 4, 5, and 6:



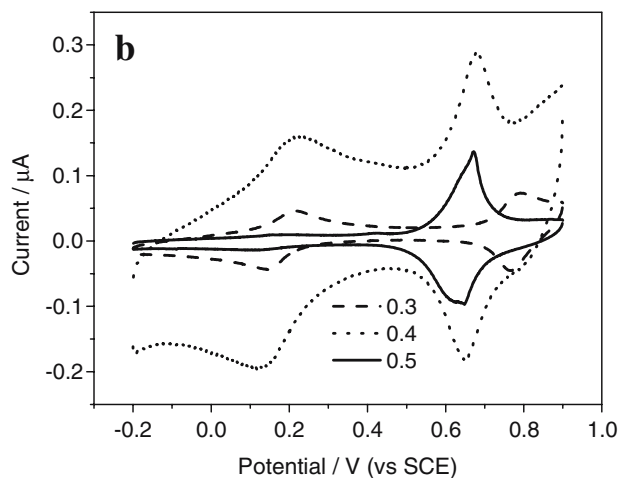
To reveal the formation mechanism of the PB film on GCPE, we employed the potentiodynamic and potentiostatic methods to study the formation process of PB. Figure 5 shows the linear potential sweep curves of a GCPE in  $0.1$  M  $K_2SO_4 + 1 \times 10^{-3}$  M  $K_3Fe(CN)_6$  (pH 1.6) or in  $0.1$  M  $K_2SO_4 + 1 \times 10^{-3}$  M  $FeCl_3$  (pH 1.6), respectively. The reduction of  $Fe^{3+}$  to  $Fe^{2+}$  and  $Fe(CN)_6^{3-}$  to  $Fe(CN)_6^{4-}$  commenced at  $0.7$  and  $0.4$  V, respectively. In the potential region between  $0.4$  and  $0.7$  V, only the reduction of  $Fe^{3+}$  to  $Fe^{2+}$  took place, and PB could only be formed through the mechanism (a). At potentials below  $0.4$  V, both the reduction reactions occurred and mechanisms (b)–(d) would be possible.



**Fig. 5** Linear potential sweep curves of a GCPE in  $0.1$  M  $K_2SO_4 + 1 \times 10^{-3}$  M  $K_3Fe(CN)_6$  (pH 1.6, dashed curve) and in  $0.1$  M  $K_2SO_4 + 1 \times 10^{-3}$  M  $FeCl_3$  (pH 1.6, solid curve), respectively. The potential was scanned from  $0.9$  to  $-0.2$  V at a scan rate of  $100$  mV/s



**Fig. 6 a** The absolute cathodic peak current for Ox/Red-1 of the PB-GCPEs as a function of the electrodeposition potential (curve *a*) and the peak current ratio of the cathodic peak currents of Ox/Red-2 to Ox/Red-1 vs the electrodeposition potential (curve *b*). The peak currents were obtained from CVs of PB-GCPEs in a blank solution of 0.1 M  $\text{K}_2\text{SO}_4$  at a scan rate of 50 mV/s. The PB-GCPEs were potentiostati-



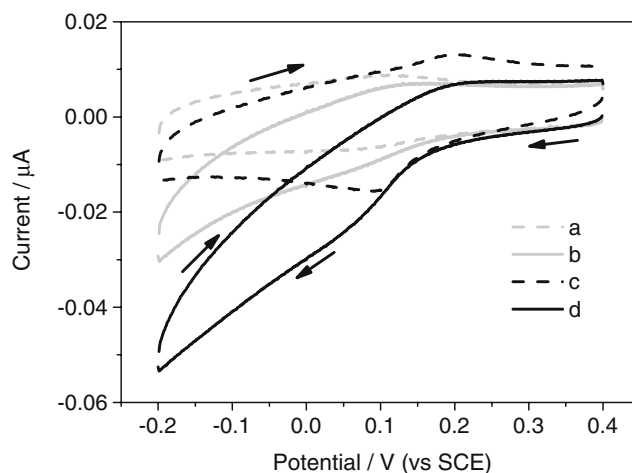
cally deposited at different potential from an acidic solution (pH 1.6) of 0.1 M  $\text{K}_2\text{SO}_4 + 1 \times 10^{-3}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  for 15 min. **b** CVs of the PB-GCPEs prepared at 0.3 V (dashed curve), 0.4 V (dotted curve), and 0.5 V (solid curve) in a blank solution of 0.1 M  $\text{K}_2\text{SO}_4$  at a scan rate of 50 mV/s

For understanding the relationship between the different electrochemical behavior of the PB-GCPEs and the possible mechanism involved in the formation process, the potentiostatic technique was employed to directly deposit PB films on GCPEs. The PB films were potentiostatically deposited on the GCPEs in the potential range of  $-0.1$ – $0.7$  V from an acidic solution (pH 1.6) of 0.1 M  $\text{K}_2\text{SO}_4 + 1 \times 10^{-3}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  for 15 min. Curve *a* in Fig. 6a shows the cathodic peak current of the Ox/Red-1 in 0.1 M  $\text{K}_2\text{SO}_4$  solution as a function of the electrodeposition potential. With the increase in the deposition potential, the peak current increased gradually. At 0.4 V, the cathodic peak current reached the maximum, which indicates the maximum formation rate of PB. This potential was much more positive than that for PB on Au or Pt electrode ( $-0.5$  and  $-0.42$  V, respectively) [19, 20]. This difference demonstrated that the cyanide adsorption on graphite substrate had little effect on the PB formation at a GCPE, and thus, most of the active sites of the GCPE were available to the PB formation.

In addition, the peak current ratio of Ox/Red-2 to Ox/Red-1 changed with deposition potential (Fig. 6a, curve *b*). With the increase in deposition potential ( $-0.2$ – $0.4$  V), the ratio increased slowly and exceeded 1 from 0.3 V (Fig. 6b). At 0.5 V, the ratio increased dramatically and was almost 12 times of the value at 0.4 V due to a synergistic effect of the increase and decrease in currents of Ox/Red-2 and Ox/Red-1, respectively (Fig. 6b). At more positive potentials, the ratio fell down to less than 1. At deposition potentials more positive with respect to 0.60 V, the peak currents for both pairs of redox couples were very small, which

indicated that less PB was formed, as ferric ions cannot be reduced at so high potentials.

We believed that the variation of the peak current ratio between Ox/Red-2 and Ox/Red-1 can be due to the different formation mechanism of PB on the GCPE surface. At potential negative with respect to 0.35 V, PB on GCPE displayed a similar electrochemistry to those on the noble metal electrodes, which implied that a similar formation process of PB occurred. In this potential region, both the ferricyanide and the ferric ions can be electrochemically reduced to ferrocyanide ions and ferrous ions, respectively. Based on the in situ electrochemical Fourier transform



**Fig. 7** Cyclic voltammograms of the PB-GCPEs in a solution of 0.1 M PBS (pH 5.4) with (curves *b* and *d*) and without 0.1 mM  $\text{H}_2\text{O}_2$  (curves *a* and *c*) at a scan rate of 50 mV/s. The PB-GCPEs were electrochemically deposited at 0.5 V (curves *a* and *b*) and 0.2 V (curves *c* and *d*) for 15 min

infrared spectroscopy results [20], PW was formed firstly at electrode surface. Thus, PB film was formed mainly via the mechanism (b) (Fig. 4). As the potential positive to 0.35 V, only ferric ions were reduced on the electrode surface; PB film was formed by the coordination of ferrous ion and ferricyanide ion around the electrode surface via the mechanism (a). The different PB formation mechanisms would lead to a possible change in the PB composition, which shows different electrochemistry.

#### Influence of deposition potential on the electrocatalytic activity of PB films

The PB–GCPEs prepared at different deposition potential show considerable difference in electrocatalytic activity towards the reduction of hydrogen peroxide. As the catalytic reduction of hydrogen peroxide originates from the PW at the electrode surface, the difference in catalytic activity of the PB films should be determined by the redox property of the PB/PW couple. To understand the influence of deposition potential on catalytic activity of PB films, two samples deposited at 0.2 and 0.5 V with high and low redox current peaks of Ox/Red-1 couple were studied. Cyclic voltammograms of a PB–GCPE towards the reduction of 0.1 mM H<sub>2</sub>O<sub>2</sub> in a 0.1 M PBS (pH 5.4) solution showed that the reduction of hydrogen peroxide started at potentials negative with respect to the reduction potential of PB to PW (Fig. 7). It was clear that the catalytic current for the reduction of hydrogen peroxide on the PB film formed at 0.2 V (curve d) was much larger than the PB film formed at 0.5 V (curve b). This phenomenon could be due to the composition or roughness of the PB films, which is undergoing.

#### Conclusions

This work presented the successful electrochemical deposition of PB films on graphite carbon paste electrodes from an acidic solution of single ferricyanide using the potentiodynamic and potentiostatic techniques. Due to the weak affinity of the GCPEs to CN<sup>-</sup> ions, the maximum formation rate of PB films was obtained at a positive potential (e.g., 0.4 V vs SCE). Different formation mechanism occurred in different deposition potential ranges. The PB formation mechanism determined the catalytic activity towards the reduction of hydrogen peroxide. This formation mechanism-dependent catalytic property of the PB films is of great significance in the construction of biosensors for the detection of various analytes.

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