Photoinducedly electrochemical preparation of Prussian blue film and electrochemical modification of the film with cetyltrimethylammonium cation

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Abstract

This work presents a photoinducedly electrochemical preparation of Prussian blue from a single sodium nitroprusside and insertion of cetyltrimethylammonium cations into Prussian blue as counter ions. The product of photoinducedly electrochemical reactions has a couple of voltammetric peaks at \( E^{0} = 0.266 \text{V} \) in 0.2 mol l\(^{-1}\) KCl solution, the measurements of X-ray powder diffraction and FT-IR spectroscopy show that it is Prussian blue (PB). The formation mechanism of a pre-photochemical reaction and subsequent electrochemical reaction is suggested. The cyclic voltammetric treatment of the freshly as-prepared PB film in 1.0 mol l\(^{-1}\) cetyltrimethylammonium (CTA) bromide solution leads to the insertion of cetyltrimethylammonium cations into the channels of Prussian blue, which substitutes for potassium ions as counter ions in Prussian blue. The Prussian blue containing CTA counter ions shows two couples of voltammetric peaks at \( E^{0} = -0.106 \text{V} \) and \( E^{0} = 0.249 \text{V} \) in 0.2 mol l\(^{-1}\) KCl solution containing 1.0 mol l\(^{-1}\) cetyltrimethylammonium bromide. Compared with the electrochemical behaviors of KFeFe(CN)\(_{6}\) in 0.1 mol l\(^{-1}\) KOH alkali solution, CTAFeFe(CN)\(_{6}\) shows relatively durable voltammetric currents due to the hydrophobic effects of cetyltrimethylammonium. The diffusion coefficients for CTA and potassium cations were estimated to be \( D_{\text{CTA}} = 1.25 \times 10^{-12} \text{cm}^{2} \text{s}^{-1} \), \( D_{\text{K}} = 2.59 \times 10^{-12} \text{cm}^{2} \text{s}^{-1} \), respectively. The peak current of electro-catalytic oxidization on hydrogen peroxide showed a linear dependence from 6.59 \times 10^{-6} \text{mol l}^{-1} to 2.20 \times 10^{-4} \text{mol l}^{-1} with \( R = 0.99947 \) (\( n = 8 \)). The linear regression equation was \( I_{p} \text{ (mA)} = 0.82949 + 0.00594C \text{ (mol l}^{-1}\) with errors of ±0.79283 \times 10^{-5} for the slope and ±0.10085 for the intercept with the detection limit of 1.46 \times 10^{-5} \text{mol l}^{-1}. Thus, it is expected to find its application in neutral or weak alkaline medium for biosensors.

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1. Introduction

Prussian blue (PB) is a prototype of mixed-valence compounds with composition of metal hexacyanoferrate (MHCF) or pentacyanotrisulfonitrilferrate (where the anion hexacyanoferrate is substituted with pentacyanotrisulfonitrilferrate, commonly known as nitroprusside). After Neff [1] and Bocarsly [2] first reported the electrochemical studies on Prussian blue and metal metallocyanide \((\text{Fe(CN)}_{6})^{3−}, \text{Ru(CN)}_{6}^{3−}, \text{Mn(CN)}_{6}^{3−}, \text{[Fe(CN)}_{6} \cdot L_{4}]^{n−}, L = \text{H}2\text{O, NO, histidine, 1,2-cyclohexyldiamine})\), respectively, these species have arisen considerable interests due to their attractive properties such as electrolytacticity [3–8], electrochromism [9–12], ion-exchange [13–17], photomagnetism [18,19], photoelectrochemical switch effect [20] and magnetoresistance effect [21]. On the basis of these properties, some biosensors [22–29], electrochemical devices [30–32], ion-sensing [33–37], and optical sensing devices [38,39] were developed. Especially, Prussian blue is often used as an artificial enzyme for the fabrication of biosensors due to its response to hydrogen peroxide released from the reaction of glucose with dioxygen in the presence of glucose oxidase under low potential conditions. This low potential could limit effectively the interference from the coexisting substances [25] such as dopamine, ascorbic acid and uric acid because these substances are easily oxidized at high potentials. Unfortunately, Prussian blue is unstable at pH > 5.0 solutions [40,41] whereas the pH value of human blood is 7.2–7.4. And Prussian blue can be dissolved during the voltammetric cycles even in neutral aqueous solutions [42] due to its high sensitivity to hydroxy, which decreases the lifetime of biosensors. Therefore, it is necessary to extend the pH range of Prussian blue and improve its stability for preparing biosensors.

The recent studies demonstrated that surfactant treatment of metal hexacyanoferrate compounds is very effective in improv-
ing their electrochemical stability. Vital and coworkers first researched the influence of cetyltrimethylammonium bromide (CTAB, cetyltrimethylammonium cation was denoted as CTA), a cationic surfactant often used in electrochemistry, on the electrochemical behaviors of Prussian blue [43–45]. And thereafter a few papers presented the influence of CTAB, polyvinyl alcohol, polyvinyl pyrrolidone, polyallylamine hydrochloride, polydiadlyl-dimethylammonium chloride and polyisostyrene sulfonate on the stability of PB and its analogues nickel or cobalt hexacyanoferrate [46–49]. Polyelectrolyte semiconductor nanoparticles composite films were prepared successfully by layer-layer self-assembly method for improving stability [50]. However, less well known is how surfactant enhances the electrochemical stability of MHCF films, whether surfactant enters into the channel of the metal hexacyanoferrate compounds, and how much the content of surfactant in the metal hexacyanoferrate compounds is (if CTA in the films). A point of view is accepted commonly that the structure of MHCF can affect the electrochemical behavior and stability, thus it is expected to obtain the structural information on surfactant improving the PB stability.

Previously, we reported the electrochemical behaviors of nanosized Prussian blue [51], LaHCF [52], and ZrHCF [53]. In the present work, we focus on a new preparation method of PB film on a sheet of indium tin oxide (ITO) transparent conductive glass by cyclic voltammetry, Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) was scanned electrochemically in an aqueous CTAB solution and the film was characterized by cyclic voltammetry, Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD) measurements, scanning electronic microscopy (SEM) and transmission electron microscope (TEM).

2. Experimental

2.1. Materials

The chemicals, KCl, K$_3$Fe(CN)$_6$ and (NH$_4$)$_2$Fe(SO$_4$)$_2$ (purchased from Beijing Chemical Reagent Factory, China), are of analytical reagent grade and used as received. The content of sodium nitroprusside (purchased from Guangzhou Chemical Reagent Factory, China) is more than 98.00%. The purity of cetyltrimethylammonium bromide (purchased from Shanghai Linfeng Chemical Reagent Co., Ltd., China), is more than 99.5%. The water used in experiments was purified with a Milli-Q system with a resistivity higher than 18.2 MΩ cm. All solutions were prepared with the deionized water.

2.2. Apparatus

Cyclic voltammetry was performed using a CHI660C electrochemical workstation (CH Instrument Company, TX, USA). The electrochemical experiments were conducted in a conventional three-electrode system. An ITO conductive glass sheet electrode was used as working electrode with resistance 11.4 Ω/sq. The ITO glass was tailored by the method mentioned according to the desired size, and was washed with deionized water first. And then, it was cleaned with alcohol in an ultrasonic cleaner for 15 min. Finally, it was rinsed thoroughly with deionized water again. If necessary, the above pre-treatment for ITO electrode could be repeated until a clean ITO electrode was obtained. Such an ITO electrode was immersed in a single sodium nitroprusside solution for electrochemical preparation of Prussian blue film under irradiation. The concentration of sodium nitroprusside solution was 1.0 × 10$^{-2}$ mol l$^{-1}$ with 0.20 mol l$^{-1}$ KCl supporting electrolyte.

A freshly as-prepared PB film was scanned immediately in 1.0 mmol l$^{-1}$ CTAB solution to characterize the influence of CTAB on PB film. The lights of wavelength 380 nm and 460 nm were obtained by a 380-cutoff filter that allows the light with the wavelength $\lambda$ > 380 nm to pass, and a 460-cutoff filter that allows the light with the wavelength $\lambda$ > 460 nm to pass, respectively.

3. Results and discussion

3.1. Photoinducedly electrochemical preparation

A clean ITO electrode was immersed in a 1.0 × 10$^{-2}$ mol l$^{-1}$ nitroprusside solution containing 0.20 mol l$^{-1}$ KCl pH 6.50 supporting electrolyte, then cyclic voltammetric sweeps were performed between −0.40 V and 0.60 V at a scan rate of 50.0 mV s$^{-1}$, the resulting cyclic voltammograms under irradiation were very different from those in dark as denoted in Fig. 1. Under illumination the voltammetric peak currents increased gradually with cyclic time whereas the voltammetric ones kept almost unchanged in the same solution in dark, suggesting the illumination induces the electrochemical reaction.

That the current increased gradually but not immediately under illumination means the current is electrochemical reaction current but is not photocurrent. The resulting film under illumination is blue seen with naked eyes, the cyclic voltammograms of the blue film electrode in 0.2 mol l$^{-1}$ KCl supporting electrolyte were shown in Fig. 2. From the Figure a couple of voltammetric peaks can be seen with an anodic peak potential at 0.330 V versus SCE and a cathodic peak potential at 0.232 V versus SCE (the formal redox potential $E^\circ = (E_{pa} + E_{pc})/2 = 0.266$ V), the potential difference of peak to peak is 68.0 mV (similar to one [45] reported by Pillai where the potential difference for Prussian blue is 80 mV), showing a non-surface control kinetic characteristics. Further studies
showed the blue film can be also obtained by cyclic voltammetry in nitroprusside solution after the solution was illuminated for 15 min. In this case the peak potentials of the resulting film for the anode and the cathode were the exact same as those under in situ illumination, suggesting the product in both cases is the same. However, the currents of voltammetric peaks cannot be obtained if a clean ITO electrode was scanned in a fresh nitroprusside solution without illumination. Moreover, the peak currents increase with the scanning cycles under irradiation of light with wavelength 380 nm whereas the currents kept almost unchanged under irradiation of light with wavelength 460 nm (see supporting materials). Thus, \([\text{Fe(CN)}_5\text{H}_2\text{O}]^{2-}\), an intermediate, was formed under irradiation of light with wavelength 360 nm [54], and it might be transferred further to Prussian blue during the potential sweep.

3.2. Stability of PB film in KCl solution

To examine the stability of the freshly prepared blue film, the electrode was scanned continuously for 20 cycles (Fig. 3) in 0.20 mol l\(^{-1}\) pH 6.5 KCl solution. The results showed that the peak current declined by 87.5% for the anodic peak, 86.1% for the cathodic peak, which indicates the PB film is not very stable in the nearly neutral medium. Therefore, the stability needs to improve.

3.3. Electrochemical treatment in CTAB solution

In order to improve the stability of the film, the as-prepared PB film on ITO electrode was immersed in 1.0 mmol l\(^{-1}\) CTAB solution containing 0.2 mol l\(^{-1}\) KCl electrolyte for 20 voltammetric cycles. The obtained voltammograms for 20 cycles were shown in Fig. 4. Fig. 4 shows the currents declined at the couple of peaks A\(_0\) and C\(_0\) during the first 10 cycles, and then peak C\(_0\) started to become bigger and bigger at the eleventh cycle. At the fifth cycle the couple of peaks A\(_1\) and C\(_1\) appeared obviously, and subsequently the couple of peaks became smaller and smaller or even disappeared. At the tenth cycle a new couple of peaks A\(_2\) and C\(_2\) started to appear, the couple of peaks A\(_2\) and C\(_2\) became stable and increased gradually during the sequential cycles. At the end two couples of voltammetric peaks appeared as shown in Fig. 5. For one couple of cyclic voltammetric peaks, the potential of anodic peak is...
electrochemical syntheses were measured. The resulting spectra of the species from both chemically and photoinducedly electro-synthesized PB are shown in Fig. 6. FT-IR spectra for Prussian blue: (A) photoinducedly electrochemical synthesis (B) and solid CTAB (C).

−0.047 V and potential of cathodic peak is −0.165 V, the formal redox potential \( E^o = −0.106 \) V in 0.2 mol l\(^{-1} \) KCl solution containing 1.0 mmol l\(^{-1} \) CTAB, the potential difference of peak to peak is 0.118 V. For the other couple of cyclic voltammetric peaks, the potentials of anodic and cathodic peaks are 0.318 V and 0.180 V, respectively, the formal redox potential \( E^o = 0.249 \) V in 0.2 mol l\(^{-1} \) KCl solution containing 0.1 mol l\(^{-1} \) CTAB, the potential difference of peak to peak is 0.138 V.

Compared with that in 0.2 mol l\(^{-1} \) KCl solution (Fig. 3), the stability of the film in 1.0 mol l\(^{-1} \) CTAB solution was improved greatly. The current data of a freshly prepared PB film electrode, ones after cyclic voltammetry in 0.2 mol l\(^{-1} \) CTAB, the potential difference of peak to peak is 0.138 V.

Table 1

<table>
<thead>
<tr>
<th>Current</th>
<th>PB film(^a)</th>
<th>PB film(^b)</th>
<th>CTA-PB film(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_p ) (( \mu A ))</td>
<td>165.7</td>
<td>22.2</td>
<td>97.6</td>
</tr>
<tr>
<td>( I_c ) (( \mu A ))</td>
<td>−157.6</td>
<td>−20.5</td>
<td>−153.6</td>
</tr>
</tbody>
</table>

\( ^a \) PB film: currents of the freshly prepared PB film in 0.2 mol l\(^{-1} \) KCl solution.
\( ^b \) PB film: currents after cyclic voltammetry in 0.2 mol l\(^{-1} \) KCl solution for 20 cycles.
\( ^c \) CTA-PB film: sum of two peak currents after cyclic voltammetry in 0.2 mol l\(^{-1} \) KCl + 1.0 mmol l\(^{-1} \) CTAB solution for 20 cycles.

In order to identify the composition of the blue film, FT-IR spectroscopy was used. The absorption at 2076 cm\(^{-1}\) was assigned to metal–carbon–nitrogen bending mode [9]. The absorption at 1940 cm\(^{-1}\) is assigned to T1u CN stretching vibration, 598 cm\(^{-1}\) is assigned to asymmetric stretching vibration, symmetric bending mode of interstitial water in PB lattice channel, respectively. A small absorption at 1391 cm\(^{-1}\) is assigned to asymmetric stretching vibration, symmetric stretching vibration, and bending mode of carbon dioxide, respectively. A small absorption at 1400 cm\(^{-1}\) indicates the presence of coprecipitated nitroprusside ions [55], which is similar to that of Prussian blue (where ferricyanide ions were coprecipitated in PB) [9].

Because photolysis of nitroprusside in aqueous solution with light of wavelength 340–430 nm forms \([\text{Fe(CN)}_5\text{H}_2\text{O}]^2^-\) [54], and the irradiation of wavelength \( \lambda = 460 \) nm did not lead to the increase of peak current in our diagnostic voltammetric experiment (see supporting materials), the mechanism of the overall reactions is suggested as follows:

**Photochemical reaction:**

\[
\text{Fe}^{III}(\text{CN})_5\text{NO} + \text{H}_2\text{O} + \text{hv} \rightarrow [\text{Fe}^{III}(\text{CN})_5\text{H}_2\text{O}]^{2-} + \text{NO}
\]

**Electrochemical reaction:**

\[
2[\text{Fe}^{III}(\text{CN})_5\text{H}_2\text{O}]^{2-} + \text{K}^+ + \text{e}^- \rightarrow \text{K}[\text{Fe}^{II}\text{Fe}^{II}(\text{CN})_6] + \text{nH}_2\text{O} + 4\text{CN}^-
\]

Here the species NO is first released on irradiation [54–60], and then, the “soluble” [48,49,61] Prussian blue containing potassium ions is formed due to the presence of an excess of potassium ions as supporting electrolyte in solution.

3.4. FT-IR characterization

3.4.1. Studies on IR spectra of synthesized PB and electro-synthesized PB

In order to identify the composition of the blue film, FT-IR spectra of the species from both chemically and photoinducedly electrochemical syntheses were measured. The resulting spectra are similar to each other as shown in Fig. 6 and displayed the unique characteristic peak of Prussian blue. The absorption at 2076 cm\(^{-1}\) is assigned to T1u CN stretching vibration, 598 cm\(^{-1}\) and 498 cm\(^{-1}\) assigned to metal–carbon–nitrogen bending mode [9]. The absorptions at 3430 cm\(^{-1}\) and 1631 cm\(^{-1}\) assigned to the stretching and bending modes of interstitial water in PB lattice channel, respectively. The absorptions at 2363 cm\(^{-1}\), 1391 cm\(^{-1}\) and 677 cm\(^{-1}\) are assigned to the anti-symmetric stretching vibration, symmetric stretching vibration, and bending mode of carbon dioxide, respectively. A small absorption at 1940 cm\(^{-1}\) indicates the presence of coprecipitated nitroprusside ions [55], which is similar to that of Prussian blue (where ferricyanide ions were coprecipitated in PB) [9].

Because photolysis of nitroprusside in aqueous solution with light of wavelength 340–430 nm forms \([\text{Fe(CN)}_5\text{H}_2\text{O}]^2^-\) [54], and the irradiation of wavelength \( \lambda = 460 \) nm did not lead to the increase of peak current in our diagnostic voltammetric experiment (see supporting materials), the mechanism of the overall reactions is suggested as follows:

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\]

**Electrochemical reaction:**

\[
2[\text{Fe}^{III}(\text{CN})_5\text{H}_2\text{O}]^{2-} + \text{K}^+ + \text{e}^- \rightarrow \text{K}[\text{Fe}^{II}\text{Fe}^{II}(\text{CN})_6] + \text{nH}_2\text{O} + 4\text{CN}^-
\]

Here the species NO is first released on irradiation [54–60], and then, the “soluble” [48,49,61] Prussian blue containing potassium ions is formed due to the presence of an excess of potassium ions as supporting electrolyte in solution.

3.5. Studies on IR spectra of CTA-PB

To elucidate the structure and composition of the film after it being scanned in CTAB solution, the infrared spectroscopic measurements were performed, the obtained IR spectra of CTA-PB, PB and pure CTAB were shown in Fig. 7. The two intense bands around 2920 cm\(^{-1}\) and 2852 cm\(^{-1}\), in both CTAB and CTA-PB, were assigned to asymmetric and symmetric stretching vibration [62] of CH\(_2\) from the methylene chain, respectively. The assignments of stretching vibrations from both CH\(_2\) in CTA and CN in PB were listed in Table 2. The finding of the methylene chain in PB film treated electrochemically in CTAB aqueous solution confirmed the presence of CTA cations in the film by comparison of IR data in Table 2. The quantitative analysis from IR spectrum of CTA-PB film has shown that the intensity ratio of peaks \( \nu_{\text{CH}_2} \) to \( \nu_{\text{CN}} \) is close to 1:1, which is in agreement with that from CTA[Fe(III)Fe(II)(CN)_6] film (see supporting materials), whereas the ratio in (CTA)_3[Fe(CN)_6] is 1:1.

![Fig. 6. FT-IR spectra for Prussian blue: (A) photoinducedly electrochemical synthesis and (B) chemical synthesis.](image)

**Table 1**

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\( ^a \) PB film: currents of the freshly prepared PB film in 0.2 mol l\(^{-1} \) KCl solution.
\( ^b \) PB film: currents after cyclic voltammetry in 0.2 mol l\(^{-1} \) KCl solution for 20 cycles.
\( ^c \) CTA-PB film: sum of two peak currents after cyclic voltammetry in 0.2 mol l\(^{-1} \) KCl + 1.0 mmol l\(^{-1} \) CTAB solution for 20 cycles.

**Table 2**

<table>
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<tr>
<th>Species</th>
<th>CH(_2) stretching vibration (cm(^{-1}))</th>
<th>CN stretching vibration (cm(^{-1}))</th>
<th>Intensity ratio of peak ( \nu_{\text{CH}<em>2} ) to ( \nu</em>{\text{CN}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB</td>
<td>2076</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTAB</td>
<td>2920, 2852</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTA-PB</td>
<td>2920, 2852</td>
<td></td>
<td>1:1</td>
</tr>
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</table>
close to 3:1. The relative ratios confirm that the molar ratio of ferri cyanide to cetyltrimethylammonium in CTA-PB is equal to 1:1. Moreover, Fe(II), CATB and Fe(CN)$_6^{3-}$ were mixed to result in a blue species, the XRD pattern of the species is consistent with that of PB (see the next section and supporting materials). Thus, CTA ions were inserted to Prussian blue and work as counter ions. The electrochemical reaction of the soluble PB in aqueous CTAB solution can be shown as follows:

$$\text{KFe}^{II}\text{Fe}^{III}(\text{CN})_6 + \text{CTA}^+ + e^- \rightarrow \text{CTAFe}^{II}\text{Fe}^{II}(\text{CN})_6 \quad (3)$$

$$\text{CTAFe}^{II}\text{Fe}^{II}(\text{CN})_6 - e^- \rightarrow \text{CTAFe}^{II}\text{Fe}^{III}(\text{CN})_6 + \text{K}^+ \quad (4)$$

CATFe$^{II}$Fe$^{III}$(CN)$_6$ was formed by reactions (3) and (4).

It is reasonable that CTA cations entered into the channels of Prussian blue as counter ions during the potential sweeps, because Prussian blue needs chargedly positive ions to maintain the electroneutrality when it is reduced to Everitt's salt. The couple of peaks A1 and C1 in Fig. 6 could be assigned to the intermediate or transition state during the electrochemical sweeps. In the case of CTA cations that worked as counter ions in PB film the chemical surroundings of electroactive components have been changed, so a new couple of peaks appeared at $E^- = -0.106$ V. In fact, the counter ions in Prussian blue film have major effects on peak potentials. For example, the peak potentials of PB film in aqueous NaCl solution are very different from those in KCl electrolyte [48].

3.6. XRD characterization

Prussian blue was synthesized from the starting materials both K$_3$Fe(CN)$_6$ and (NH$_4$)$_2$Fe(SO$_4$)$_2$. They were mixed equivalently, the classic volume of each is 30 mL in the concentration of $1.0 \times 10^{-2}$ mol l$^{-1}$ in the presence of 0.2 mol l$^{-1}$ KCl. It should be noted that the PB synthesized chemically is under conditions in an excess of potassium ion, which is similar to the case of the photoinducedly electrochemical synthesis of the blue film. Thus it ensures the formation of the soluble Prussian blue containing potassium ions [48,49].

The blue powder (A) photoinducedly electro-synthesized, Prussian blue (B) synthesized chemically, and CTA-PB (C) (the synthetic procedure can be seen in supporting materials) were detected with X-ray powder diffraction. The resulting diffraction patterns were shown in Fig. 8 as follows.

The XRD measurements showed these three species possess the similar diffraction pattern, the diffraction angle positions of 2θ in Table 3. Thus, the data of XRD confirmed the product of photoinducedly electrochemical reaction is Prussian blue and CTA cations were inserted into the PB channels.

3.7. Film morphological observations

The morphology of the as-prepared PB sample was characterized by SEM. Fig. 9 shows the imagines of the as-prepared PB particles amplified by 20000 times before (a) and after (b) it was treated electrochemically in 1.0 mmol l$^{-1}$ CTAB solution. The difference between (a) and (b) in Fig. 9 is that the small convex shapes like bean can be clearly seen from the freshly prepared PB film, whereas they became flat after the film was scanned electrochemically in CTAB solution. Compared with PB film prepared by the traditional electrochemical method, the present PB film is more

Table 3

<table>
<thead>
<tr>
<th>PB</th>
<th>2θ (°)</th>
<th>d (Å)</th>
<th>d (Å)</th>
<th>d (Å)</th>
<th>d (Å)</th>
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<td>17.39</td>
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<td>3.61</td>
<td>2.55</td>
<td>2.27</td>
<td>1.80</td>
<td>1.69</td>
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<tr>
<td>CTA-PB</td>
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<td>5.13</td>
<td>3.61</td>
<td>2.55</td>
<td>2.27</td>
<td>1.82</td>
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<td>210</td>
<td>220</td>
<td>221, 300</td>
<td>14</td>
<td>13</td>
</tr>
</tbody>
</table>
uniform. The TEM observations displayed that the small convexes are the nano-particles with the diameter of 20–30 nm as shown in Fig. 10.

### 3.8. Electrochemical behaviors of CTA-PB film and diffusion coefficients

The obtained CTA-film electrode was immersed in 0.2 mol l\(^{-1}\) KCl solution containing 1.0 mmol l\(^{-1}\) CTA for the electrochemical characterization at different scan rates, the resulting voltammetric curves were shown in Fig. 11. The corresponding plots of anodic peak currents versus square roots of scan rates were shown in Fig. 12. The figure indicates the anodic peak currents versus square roots of scan rates have a good linear relationship, the linear correlation coefficient is \( R = 0.99938 \) for CTA and \( R = 0.99949 \) for potassium, respectively, suggesting both electrochemical reduction processes are under diffusion control, which is in good agreement with that of Prussian blue [9]. The concentration of PB on ITO surface was calculated to be 1.48 × 10\(^{-3}\) mol cm\(^{-3}\). Thus, the peak height is given by the Randles–Sevcik equation [64,65]

\[
i_p = 2.69 \times 10^5 n^{1/2} A D^{1/2} C^{1/2}
\]

where \( i_p \) is the peak current in amperes, \( n \) the electron transfer number, \( A \) the electrode area in cm\(^2\), \( D \) the diffusion coefficient in cm\(^2\) s\(^{-1}\) and \( v \) the scan rate in Vs\(^{-1}\). On the basis of the slope of \( i_p \) versus \( v^{1/2} \) plot in Eq. (6) one can calculate the apparent diffusion coefficient of both CTA and potassium inside the CTA-PB film. For CTA ions, \( D_{\text{CTA}} \) is 1.25 × 10\(^{-12}\) cm\(^2\) s\(^{-1}\) and \( D_K \) is 2.59 × 10\(^{-12}\) cm\(^2\) s\(^{-1}\) for potassium ions. It is to be noted that the \( D \) values obtained are comparable to those obtained for PB film by other methods [66].

### 3.9. Stability of CTA-PB in alkali medium

The as-prepared CTAFe\(^{III}\)Fe\(^{II}\)(CN)\(_6\) electrode is very stable, the peak current can still keep even in 0.1 mol l\(^{-1}\) KOH electrolyte for 20 potential cycles, the current drop is only 22.5% denoted as Fig. 13. However, the voltammetric peak current of Prussian blue (it was prepared by popular potential sweeps between −0.2 V and 1.0 V for 5 cycles in 1.0 mmol l\(^{-1}\) FeCl\(_3\) + 1.0 mmol l\(^{-1}\) K\(_3\)Fe(CN)\(_6\) containing 0.2 mol l\(^{-1}\) KCl solution) disappeared immediately. Therefore, CTA ions improve greatly the stability of Prussian blue in alkali solution. The improvement is assigned to hydrophobicity from CTA as counter ions in film. Because Prussian blue is very sensitive to hydroxy, it will be broken down when it is in touch with OH\(^-\) and form Fe(OH)\(_3\) as follows:

\[
K\text{Fe(Fe(CN))}_6 + 3\text{OH}^- = \text{Fe(OH)}_3 + \text{Fe(CN)}_6^{4^-} + K^+
\] (7)

The hydrophobic CTA prevents PB from hydroxy and leads to relative stable voltammetric peaks.
The determination of the H$_2$O$_2$ concentration can characterize the concentration of hydrogen peroxide from 6.59 × 10$^{-6}$ to 2.20 × 10$^{-4}$ mol l$^{-1}$ with R = 0.99947, and the stability of CTAFe(CN)$_6$ film improves greatly in 0.1 mol l$^{-1}$ KOH aqueous solution due to the hydrophobic effects of cetyltrimethylammonium, it is expected to find its application in aqueous neutral or weak alkali medium for biosensors.

**4. Conclusions**

Prussian blue can be prepared by photoinducedly voltammetry from a single sodium nitroprusside. The formation mechanism is photochemical reaction first and subsequently electrochemical reaction. The cetyltrimethylammonium cations can enter into the channels of the Prussian blue as counter ions during voltammetric sweeps, as a result, CTAFe(CN)$_6$ is formed. The diffusion coefficients for CTA and potassium cations were estimated to be $D_{CTA} = 1.25 × 10^{-12}$ cm$^2$ s$^{-1}$ and $D_K = 2.59 × 10^{-12}$ cm$^2$ s$^{-1}$, respectively. Because the peak current showed a linear dependence on hydrogen peroxide concentration from 6.59 × 10$^{-6}$ to 2.20 × 10$^{-4}$ mol l$^{-1}$ with $R = 0.99947$, and the stability of CTAFe(CN)$_6$ film improves greatly in 0.1 mol l$^{-1}$ KOH aqueous solution due to the hydrophobic effects of cetyltrimethylammonium, it is expected to find its application in aqueous neutral or weak alkali medium for biosensors.

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**Appendix A. Supplementary data**


**References**