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Potentiodynamic deposition of Prussian blue from a solution containing single component of ferricyanide and its mechanism investigation

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Abstract Potentiodynamic techniques were used for the direct electrodeposition of Prussian blue nano-clusters from an acidic solution of ferricyanide. Electrochemical, EQCM, IR, AFM, and UV/vis measurements were carried out to characterize deposited nano-sized Prussian blue and to explore the formation mechanism. Results showed that ferricyanide could partially dissociate to free ferric and cyanide ions. The driving force of this dissociation is the formation of PB and the evolution of HCN. The optimal potential window for the potentiodynamic formation of PB from an acidic solution (pH 1.6) is between -0.5 V and 0.4 V. In addition, the influence of surface adsorption of CN^- ions on the formation of PB was discussed.

Keywords Prussian blue · Nano-clusters · Ferricyanide · Electrodeposition · Mechanism · Surface chemistry

Introduction

The highly insoluble polymeric inorganic semiconductor Prussian blue (PB) has fascinated a school of scientists ever since its invention several hundred years ago due to its attractive electrochromic property, catalytic activity, easy preparation, and low cost. In addition, PB and its analogues have found promising applications in various fields, i.e., electrocatalysis [1, 2], ion selectivity [3], electrochromism [4], photoresponse [5], solid-state batteries [6], sensors and biosensors [7, 8], and magnetic devices [9, 10, 11].

Dedicated to Prof. Wolf Vielstich on the occasion of his 80th birthday in recognition of his numerous contributions to interfacial electrochemistry

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Various methods for the preparation of PB or its analogues film have been reported, i.e., chemical or electrochemical deposition PB from a solution containing free metallic ions and metalcyanide ions, dip-coating or casting PB from a PB colloidal solution. However, application of these methods is usually hampered by poor control of the PB film at nanometer level. To overcome the above disadvantage, surface assembly techniques have been attempted. Langmuir-Blodgett (LB) technique uses charged surfactant as template to control the nucleation and to orientate the growth of PB analogue monolayer at the interface between surfactant and aqueous solution [12]. Self-assembly deposition based on multiple successive absorptions of free metallic and metalcyanide ions is also suitable for preparation of PB film with nanometer precision [13]. Obviously, all these methods mentioned above for the preparation of PB or its analogues require the simultaneous existence of free metallic ions and ferricyanide/ferrocyanide ions in solutions with an excess of supporting ions, such as K^+ , NH_4^+ , Rb^+ , and Cs^+ [14]. In this paper we introduce a concept of one-step electrodeposition of densely packed ultrathin film of Prussian blue nano-clusters (nano-PB) with a thickness in nanometer range from an acidic solution containing only ferricyanide and potassium sulfate. The formed nano-PB layers were characterized with voltammetry, reflection infrared spectroscopy and atomic force microscope. The influence of solution pH, surface chemistry of electrodes and various electrochemical parameters on the formation kinetics of nano-PB layers has been investigated. Electrochemical Quartz Crystal Microbalance (EQCM) and UV/vis measurements were performed to obtain information on the formation mechanism of nano-PB. Pt and Au electrodes have been used to investigate the importance of the surface chemistry to the formation of PB.

Experimental

Chemicals Ferricyanide and other chemicals were of analytic reagent grade. All the chemicals were used as received without

further purification. Twice distilled water was used throughout this work. The pH value of the Clark-Lubs buffers containing single component of ferricyanide was adjusted using 1 mol/l HCl solution.

Instrumentation Electrochemical measurements were performed with a CHI650 Electrochemical Workstation (CH Instrument, USA). A traditional three-electrode electrochemical cell was used for electrochemical measurements. A saturated calomel electrode (SCE) and platinum sheet were used as reference electrode and counter electrode, respectively. Electrochemical Quartz Crystal Microbalance (EQCM) experiments were carried out with an Autolab Modular picobalance Instrument (Eco Chemie, Utrecht, The Netherlands).

The absorption spectra of ferricyanide solutions were recorded with a UV/vis spectrophotometer (Shimadzu, Japan). The reflection IR spectrum was measured with a Nicolet 170X Fourier IR spectrometer (Nicolet, USA). The AFM experiments were performed with SPA-300 HV (Seiko, Japan).

IR experiment Two hundred times cyclic potential sweeps of a gold sheet (geometric area: $5 \times 6 \text{ mm}^2$) between -0.2 V and 0.9 V (vs SCE) in a solution (pH 1.6) containing ferricyanide were carried out for electrodepositing PB film. Before the reflection IR spectra were collected, the PB modified gold electrode was carefully washed with water and dried with nitrogen gas.

Results and discussion

Potentiodynamic deposition of Nano-PB clusters

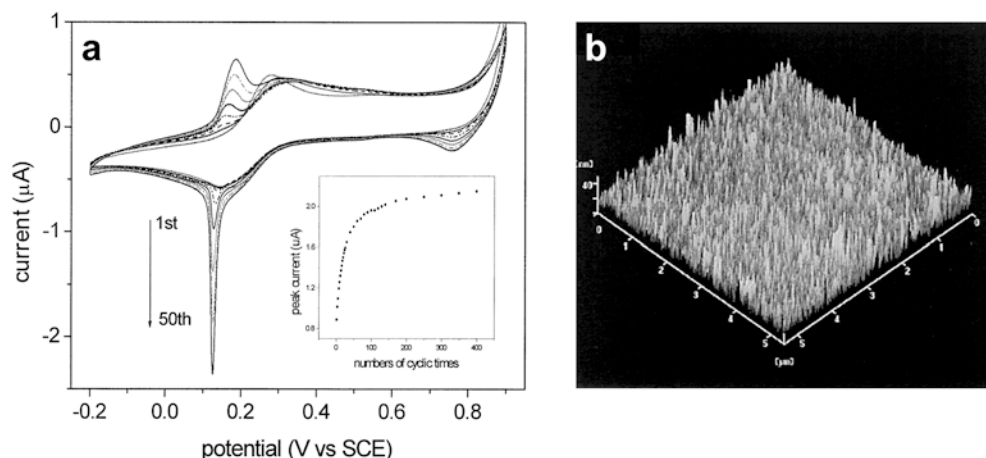
Figure 1a shows cyclic voltammograms of a gold electrode from a freshly prepared acidic solution (pH 1.6) of $0.1 \text{ mol/l K}_2\text{SO}_4 + 1 \times 10^{-3} \text{ mol/l K}_3\text{Fe}(\text{CN})_6$. In addition to the typical diffusion-controlled current peaks of ferricyanide/ferrocyanide couple, two new pairs of peaks located at 0.17 V and 0.84 V appeared. The current of the new peaks increased dramatically with the increase of the potential scanning time. Reflection IR result demonstrates that the surface species formed electrochemically exhibits the same absorption bands of PB. The absorption band at 2071 cm^{-1} is the common characteristic of PB and its analogues, corresponding to the stretching vibration of the CN^- group [15]. Absorption bands at 597 cm^{-1} and 498 cm^{-1} are due

to the formation of $\text{M-CN-M}'$ [16]. The absorption bands at 3400 cm^{-1} and 1600 cm^{-1} are attributed to the O-H stretching mode and H-O-H bending mode, respectively, indicating the presence of interstitial water in the compound [17]. Potential scanning in various potential windows was performed to obtain optimum potential range for PB formation in the acidic ferricyanide solution (pH 1.6). It was found that the peak current of PB decreased dramatically when the upper potential limit of the potential window was higher than 1.0 V . This is mainly due to the formation of surface oxide of the Au substrate. Set the upper potential limit lower than 1.1 V , the peak current of PB increased with negative shift of the lower potential limit. Experimental results showed that cyclic potential scanning in the potential range of -0.5 to 0.4 V (vs SCE) gave the highest PB current, indicating maximum amount of PB could be formed since the peak current is directly proportional to the surface coverage of the PB formed on electrodes. The isotherm for the potentiodynamic growth of nano-PB in the potential range of -0.5 V to $+0.4 \text{ V}$ (vs SCE) at a scan rate of 100 mV/s is shown as the inset in Fig 1a. Obviously, the peak current increases rapidly in the first 50 cycles. It then tends to a constant value up to 300 cycles, indicating a full layer of PB was formed. Tapping mode AFM characterization displays that the nano-PB clusters distributed uniformly in the full layer and the film thickness was no more than 50 nm (Fig. 1b). This result hints that the formation of nano-PB clusters might occur via a homogeneous nucleation and growth mechanism.

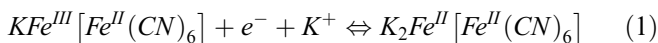
The electrochemical behavior of prepared nano-PB film

After 50 cyclic potential scans of an gold electrode in an acidic solution (pH 1.6) of $0.1 \text{ mol/l K}_2\text{SO}_4 + 1 \times 10^{-3} \text{ mol/l K}_3\text{Fe}(\text{CN})_6$ at a scan rate of 100 mV/s , a cyclic voltammogram of the PB film modified gold electrode in a blank solution of $0.1 \text{ mol/l K}_2\text{SO}_4$ at the scan rate was recorded. The current-potential curve displays typical

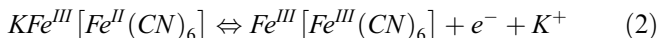
Fig. 1 a Cyclic voltammograms of a gold electrode in a solution of $1 \times 10^{-3} \text{ mol/l Fe}(\text{CN})_6^{3-} + 0.1 \text{ mol/l K}_2\text{SO}_4$ (pH 1.6) at the 1st, 3rd, 5th, 10th, 20th, 30th, 40th, and 50th potential scans with a scan rate of 100 mV/s . The inset shows a plot of the cathodic peak current at 0.17 V vs the cyclic number of potential scan. **b** Three-dimensional Tapping-mode DFM image ($5 \mu\text{m} \times 5 \mu\text{m}$) of the PB nano-cluster film



redox characteristics of PB modified electrode. The pair of peaks located at 0.17 V corresponds to the reduction of PB to Prussian White (Eq. 1):



while the pair of peaks centered at 0.84 V refers to the oxidation of PB to Berlin Green (Eq. 2):



A linear relationship of the anodic and the cathodic peak currents of PB as a function of the scan rate between 2 and 25 mV/s was observed, indicating that the observed electrochemical reactions are surface processes. At higher scan rates up to 500 mV/s, the peak currents were proportional to the square root of the scan rate, indicating the reaction kinetics change from surface processes to solution diffusion-limited processes. These results are in good agreement with those reported previously [18].

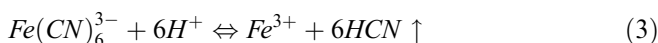
It is known that PB has a zeolitic structure, in which ions or water molecules at the interstitial sites can be involved. Certain cations [14], such as K^+ , NH_4^+ , Rb^+ , and Cs^+ , could be the counter ions required for maintaining electroneutrality of PB film as it undergoes redox reaction. EQCM measurements were performed to investigate the redox switching behavior of the prepared nano-PB film. Figure 2 shows a stable cyclic voltammogram and the simultaneously recorded EQCM response during the electrodeposition of nano-PB film on a gold electrode from an acidic solution (pH 1.6) of 0.1 mol/l $K_2SO_4 + 1 \times 10^{-3}$ mol/l $K_3Fe(CN)_6$. For obtaining a better resolution of EQCM response, a scan rate of 10 mV/s was used. In the potential region between -0.4 and 0.1 V, the decrease in current is due to the evolution of hydrogen, although no obvious corresponding frequency change was observed. As the potential moved more positive, accompanying the increase of the current corresponding to the oxidation of Prussian White to PB (Eq. 2), an increase in the simultaneously recorded frequency was observed. This increase in frequency indicates the decrease in mass on the crystal surface. This phenomenon is due to the outflux of K^+

cations from the PB film into solution. During the cathodic potential scan, a cathodic current due to the reduction of PB to Prussian White (Eq. 1) and a decrease in the frequency were observed. In this case, the decrease in frequency should be due to the influx of K^+ ions from solution into the zeolitic structure of PB for electroneutralization. These results are consistent with the direct participation of K^+ in the redox processes of PB for preserving its electroneutrality of the system [19].

In the traditional methods, extensive cycling of the PB film in K_2SO_4 blank solution is required in order to obtain a stable CV response. In our case, this pretreatment is not necessary. The electrochemically formed PB film is very stable in the potential region between -0.1 V and 0.9 V. Repetitive potential sweeps of the modified electrode in a blank solution of 0.1 mol/l K_2SO_4 at a scan rate of 100 mV/s for 3 h showed only a slight decrease (ca. 5%) in the peak currents of PB. The results conform that the densely packed thin film has good adhesion on the gold substrate.

The formation mechanism of PB

At first sight, the formation of PB from a solution containing single component of ferricyanide seems impossible, since another counter component, ferric ion or ferrous ion is absent in the system. In our case, the source for providing free metallic ions can only be the dissociation of ferricyanide. Therefore, UV/vis spectroscopic measurements were performed to study the stability of ferricyanide in acidic solutions. Results showed that the absorption bands of ferricyanide decreased dramatically with the storage time of the acidic solution (as shown in Fig. 3a). Since we did not observe any other new UV/vis absorption feature beside the decrease of the absorption intensity of the UV/vis features of ferricyanide, the reduction of ferricyanide ion to ferrocyanide ion or other product can be ruled out. The dramatic decrease of the UV/vis absorption intensity of ferricyanide can only be due to the dissociation of ferricyanide according to Eq. (3). Since Eq. (3) is thermodynamically unfavorable, the driving force must be provided by the evolution of HCN (*caution: all the experiments should be performed carefully*) and the formation of PB in acidic solutions:



Obviously, the presence of hydrogen ions in the solution will strongly move the equilibrium of Eq. (3) to the right side, resulting in the enhanced dissociation of ferricyanide and a reasonable concentration of ferric ions for the formation of PB. This phenomenon was exactly observed in our measurements. On the contrary, in the case of a neutral solution (pH 7.0), only a slightly decrease in the UV/vis intensity of the adsorption bands of ferricyanide was observed in the first two days (Fig. 3b, comparing the solid curve for the freshly

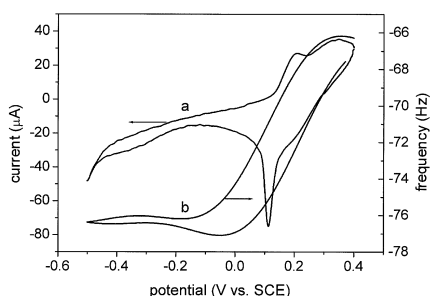
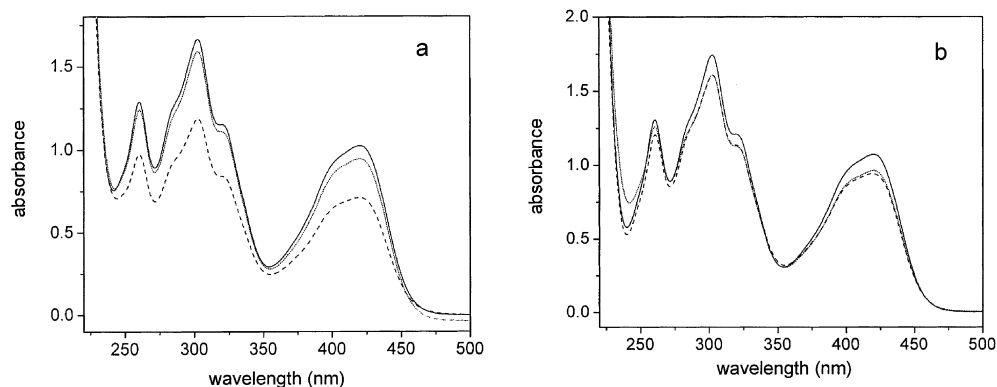


Fig. 2 a Cyclic voltammogram. b Simultaneously recorded EQCM frequency response of a gold electrode in an acidic solution (pH 1.6) of 0.1 mol/l $K_2SO_4 + 1 \times 10^{-3}$ mol/l $K_3Fe(CN)_6$ at a scan rate of 10 mV/s. The potential scan was started at 0.0 V

Fig. 3a,b UV/vis spectra of a solution of 1×10^{-3} mol/l $\text{Fe}(\text{CN})_6^{3-}$ + 0.1 mol/l K_2SO_4 for different storage time. Solution pH value: **a** 1.6; **b** 7.0. Curves from the top to the bottom correspond to the solution stored for 0 day (solid curves), 2 days (dotted curves) and 11 days (dashed curves), respectively



prepared solution with the dotted curve for two days storage time). At longer storage time of the solution, no further decrease in the UV/vis intensity appeared.

The influence of pH on the formation rate of nano-PB film

As described above, more Fe^{3+} ions could be produced from a strong acidic solution via the dissociation of ferricyanide. This phenomenon was indeed observed in our electrochemical experiments. After a gold electrode experienced 50 times cyclic potential sweeps between -0.2 V and 0.8 V in ferricyanide solutions with different pH, cyclic voltammograms of the PB modified electrode in a blank solution of 0.1 mol/l K_2SO_4 were recorded at a scan rate of 100 mV/s. Plot of the cathodic peak current at 0.17 V of the CVs as a function of the solution pH is shown in Fig. 4. The maximum peak current for a solution with pH 1.6 indicates a maximum formation rate of PB. Beyond this pH value, the formation rate of PB decreased. At $\text{pH} < 1.6$, the formation rate of PB decreased rapidly, while at $\text{pH} > 1.6$, it decreased exponentially with the solution pH. No PB formation could be observed when the solution pH was higher than 7.0 (e.g., in alkaline solution). One of the reasons is the slow dissociation of ferricyanide in alkaline solution; the other one can be attributed to the damage of PB structure in alkaline solution as suggested by Karyakin et al. that PB film can be destroyed by the aggregation of OH^- ions [20].

The influence of CN^- ions adsorption on the PB formation

Since the dissociation rate of ferricyanide ions is limited by its dissociation equilibrium constant, the dissociated free ferric ions at electrode surface should be immediately depleted even at a very low overpotential. Therefore, a potential independent formation rate of PB at electrode surface should be expected by assuming a constant dissociation rate of ferricyanide. However, our results showed that the electrode potential

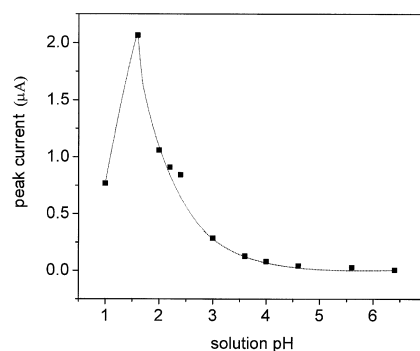


Fig. 4 Influence of solution pH on the cathodic peak current at 0.17 V of a PB film prepared electrochemically from a solution of 1×10^{-3} mol/l $\text{Fe}(\text{CN})_6^{3-}$ + 0.1 mol/l K_2SO_4 . The peak currents were obtained from the 50th CV at 100 mV/s

has a strong influence on the formation rate of PB even at potentials negative to the thermodynamic equilibrium potential (TRP) of ferric/ferrous redox couple. In these measurements, the nano-PB films were electrodeposited potentiostatically at potentials negative to TRP from an acidic solution (pH 1.6) of 0.1 mol/l K_2SO_4 + 1×10^{-3} mol/l $\text{Fe}(\text{CN})_6^{3-}$ for 15 min. Then cyclic voltammograms of the modified electrodes in a blank solution of 0.1 mol/l K_2SO_4 were recorded at a scan rate of 100 mV/s. The result is shown in Fig. 5. At potential positive to TRP, no PB formation was observed. This result is certainly expected, since the counter component, e.g., ferrous ions are absent in the solution. At potentials negative with respect to TRP, the formation rate increased exponentially with the negative shift of the deposition potential due to the reduction of ferricyanide ions in solution and the dissociated ferric ions to ferrocyanide ions and ferrous ions, respectively. At a deposition potential of -0.5 V, a maximum formation rate of PB was achieved. Interestingly, as the potential moved more negatively, the formation rate decreased dramatically with the decrease of deposition potential.

In many cases, anions can specifically adsorb on noble metal electrodes via electron feedback modes. Their adsorption behavior is strongly influenced by the

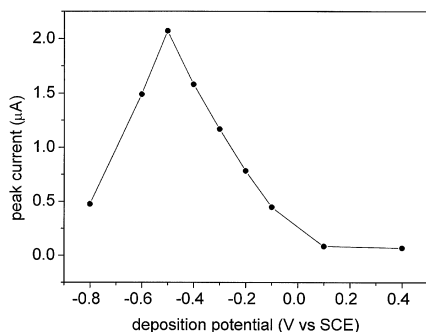


Fig. 5 The cathodic peak current at 0.17 V of a nano-PB modified electrode as a function of the electrodeposition potential. The peak currents were obtained from CVs of nano-PB modified electrodes in a blank solution of 0.1 mol/l K_2SO_4 at a scan rate of 100 mV/s. The nano-PB modified electrodes were potentiostatically deposited from an acidic solution (pH 1.6) of 0.1 mol/l $\text{K}_2\text{SO}_4 + 1 \times 10^{-3}$ mol/l $\text{K}_3\text{Fe}(\text{CN})_6$ for 15 min

potential exerted on the substrates. It is reported that CN^- ion strongly adsorbs on Pt or Au electrode surface over a wide potential range [21, 22]. The adsorption of CN^- must have strong influence on the formation of nano-PB. On one hand, the adsorption of CN^- occupies the electro-active sites available on the metal substrate, which will inhibit the electrochemical reduction of both ferricyanide ions and dissociated ferric ions. On the other hand, the adsorbed CN^- ions can immediately coordinate with the dissociated ferric ions and its reduction state-ferrous ions. The followed reaction of these free ferric and ferrous ions for the formation of nano-PB will be evidently blocked. Spectroscopic results showed that at relatively positive potentials CN^- adsorbs on the Pt electrode surface in an on-top adsorption mode via the carbon atom. Such an on-top adsorption mode changed to flat adsorption mode when the potential was made more negatively (e.g., $> -0.6\text{V}$, vs SCE) [21]. Such a change in adsorption mode hints lower interaction energy between the cyanide ion and the substrate at more negative potentials due to a decreased capability of the substrate attracting electrons from cyanide ion and a repulsion of the C end of the adsorbed cyanide away from the negatively charged electrode surface as well. A decrease in the surface coverage of adsorbed cyanide with decrease of the potential in the range of 0.25 V to -1.5 V (vs SCE) was reported based on the radioactive labeling measurements [23]. Desorption of cyanide from the electrode surface results in more free surface active sites available for the PB formation, which is also observed in our experiments (Fig. 5). At more negative potentials the desorption of adsorbed cyanide occurs more completely. Based on this result, an increased formation rate of PB could be expected. However, at potentials negative to -0.5 V hydrogen gas evolution starts. The evolution of hydrogen gas again decreases the surface active sites, in turn inhibits the deposition of PB on the substrate, resulting in the decreased formation rate of PB (Fig. 5). Since CN^-

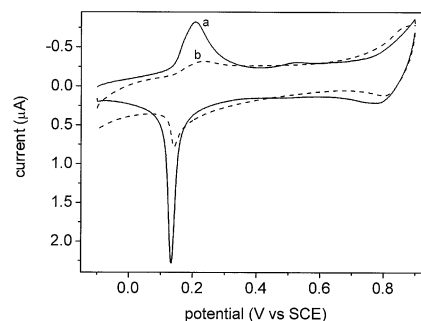


Fig. 6 a,b Cyclic voltammograms of PB film: **a** on Au electrode; **b** on Pt electrode in a solution of 0.1 mol/l K_2SO_4 . The PB films were deposited potentiodynamically from an acidic solution (pH 1.6) of 0.1 mol/l $\text{K}_2\text{SO}_4 + 1 \times 10^{-3}$ mol/l $\text{K}_3\text{Fe}(\text{CN})_6$ for 300 cycles at a scan rate of 100 mV/s

ions interact with Pt electrode more strongly than with Au, desorption of CN^- ions from Pt surface should be more difficult than from Au surface. Therefore, the formation of PB on Pt is more difficult than on Au electrode, as observed in our experiments (Fig. 6). Curves a and b show the typical cyclic voltammograms of PB deposited potentiodynamically on Au and Pt substrates from an acidic solution (pH 1.6) of 0.1 mol/l $\text{K}_2\text{SO}_4 + 1 \times 10^{-3}$ mol/l $\text{Fe}(\text{CN})_6^{3-}$, respectively. The peak current of PB observed in curve a was significantly higher than that of in curve b, indicating the strong influence of surface chemistry on the formation of PB from an acidic solution containing single component of ferricyanide.

Conclusions

The present work shows that a compacted PB film with nanostructure can be electrodeposited from an acidic solution of ferricyanide ions by potentiodynamic technique. The surface coverage of nano-PB in the range of sub-monolayer to full monolayer can be precisely adjusted by controlling the solution pH, the electrodeposition potential or the electrodeposition time. The formation of nano-PB is believed to occur via a homogeneous nucleation and growth mechanism. Dissociation of ferricyanide and reduction of the dissociated free metallic ions and ferricyanide ions in solution are the key points for meeting the prerequisites of the PB formation. The driving force for the dissociation of ferricyanide is provided by both the formation of PB and the evolution of HCN. The adsorption of CN^- ions on the electrode surface severely blocks the formation of PB from a solution containing ferricyanide and potassium sulfate. Further applications of our method in the fields of biosensors, electrochromism devices and ion sieves are in progress.

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