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Ultrathin Layers of Densely Packed Prussian Blue Nanoclusters Prepared from a Ferricyanide Solution

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Prussian Blue (PB) and its analogues form an important class of insoluble, mixed-valence compounds. Recently, there have been extensive studies for applications in magnetic materials,[1−3] molecular sieves,[4] catalysis,[5] solid-state batteries,[6] electrochromic devices,[7] biosensors,[8,9] and molecular magnets.[10] To exploit fully the applications of PB in the above fields, thin films in the nanometer range with controllable morphology are usually required. Traditional methods for the deposition of PB and its analogues on various conductive substrates require the simultaneous presence of metal ions and the corresponding metal-cyanide ions in solution with an excess of supporting cations.[11,12] However, direct electrodeposition of ultrathin PB films by controlling the concentrations of the metal and metal-cyanide ions in solution is difficult; thick and loose films usually result, with poor adhesion.[12] Recently, a method based on sequential adsorption of positively and negatively charged ions for ultrathin film formation was shown to be effective.[13−15] The thickness of the PB film could be tailored by controlling the sequence of successive adsorption steps of the metal and metal-cyanide ions.

Here, we report on an alternative electrochemical approach to the formation of an ultrathin layer of PB nanoclusters from an acidic solution of a ferricyanide salt at potentials negative with respect to the equilibrium potential of the ferric/ferrous redox couple (EP). PB is formed as a result of the dissociation of ferricyanide ions. The slow dissociation of the complex ensures a limited concentration of free ferric ions essential for the formation of a compact and defect-free ultrathin PB layer. Our method is convenient and fast; for example, a PB nanocluster film can be deposited in a few minutes. In addition, we describe promising results for enhanced detection of potassium ions and H_2O_2 with these films.

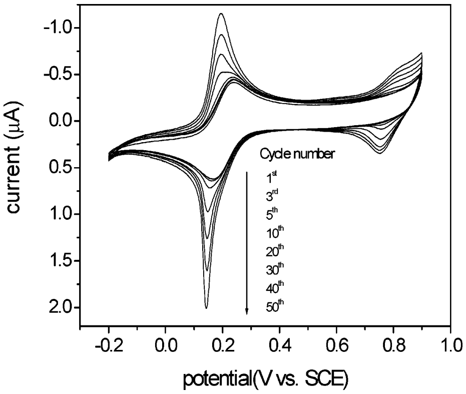

Figure 1. Cyclic voltammograms (CV) of a gold electrode in a solution (pH 1.6) of 1×10^{-3} M $Fe(CN)_6^{3-}$ + 0.1 M K_2SO_4 at a scan rate of 100 mV/s.

Potentiodynamic and potentiostatic techniques are used for the direct deposition of an ultrathin layer of PB on a gold electrode from an acidic solution (pH 1.6) containing only ferricyanide.[16] Cyclic voltammograms in the potential range −0.2 to 0.9 V (vs SCE) show the typical diffusion-limited current−potential characteristics of ferricyanide only in the first cycle of the potential scan. In the following potential sweeps, two new pairs of current peaks appear and the current increases with the number of scans (Figure 1). The cathodic current peaks are located at 0.17 and 0.84 V. The pair of peaks centered at 0.17 V corresponds to the reduction of PB to Prussian White, while the pair of peaks centered at 0.84 V refers to the oxidation of PB to Berlin Green.[17] These reactions are accompanied by mass changes due to the transfer of K^+ cations into/out of the PB film to preserve its electroneutrality.[18] For a neutral solution solution, only a very small cathodic current peak at 0.17 V was visible; the anodic current peak was evidently embedded in the diffusion-controlled current peak of ferricyanide. The reflection FTIR spectrum of the electrodeposited film in Figure 1 is the same as that reported for PB.[19−21] An absorption band at 2071 cm^{-1} is due to the stretching vibration of the CN^- group in PB. Absorption bands at 597 and 498 cm^{-1} are due to the formation of M−CN−M′. Absorption bands at

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(16) pH value of the ferricyanide solution plays a key role in the PB formation rate. Electrochemical measurements showed that an optimal solution pH for the fast electrodeposition of PB nanoclusters ultrathin film is 1.6.

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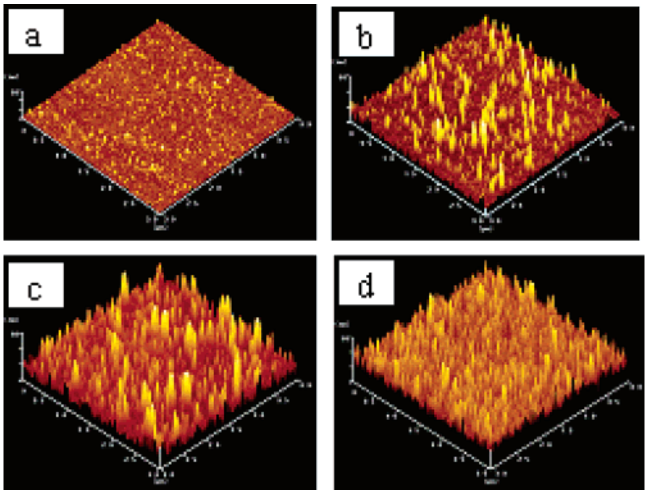

Figure 2. Three-dimensional tapping mode AFM images (3 × 3 μm) of the PB nanocluster films prepared by potentiostatic deposition in a ferricyanide solution (pH 1.6) at −0.5 V (vs SCE) for (a) 0 s, (b) 15 s, (c) 70 s, and (d) 250 s.

3400 and 1600 cm^{-1} can be attributed to the O−H stretching and H−O−H bending modes, respectively, indicating the presence of interstitial water in the compound. Extensive voltammetric studies showed that the most favorable potential for the deposition of PB is in the range of −0.5 V to ca. +0.4 V.

The influence of deposition potential on the PB formation kinetics was also studied. In these experiments, cyclic voltammograms of the deposited PB film were recorded in a blank solution of 0.1 M K_2SO_4 at a scan rate of 100 mV/s after 15 min of deposition at potentials negative with respect to the reduction potential (EP) of ferric ions in an acidic solution (pH 1.6) of ferricyanide. Results showed that at potentials positive of the EP, no PB formation was observed. When the potential was more negative than EP, the PB formation rate increased exponentially. At −0.5 V, a maximum PB formation rate is reached. With further negative shifting of the deposition potential, the PB formation rate decreased again due to the strong evolution of hydrogen.

Figure 2 shows a series of AFM images for the growth of PB ultrathin films on a gold film sputtered on glass slides. The films were potentiostatically deposited at −0.5 V in an acidic ferricyanide solution (pH 1.6) for different deposition times. For comparison, an AFM image of a bare gold film is shown in Figure 2a. There are some gold clusters (bright dots), 15 nm in diameter and 16 nm in height, distributed over the flat gold surface. After electrodeposition for 15 s, PB nanoclusters can be clearly observed (Figure 2b). With an increase of the deposition time (e.g., 70 s), the concentration of PB nanoclusters increases rapidly, although voids and defects are still present in the film (Figure 2c). With a deposition time of 250 s, all voids and defects are filled, and a densely packed PB film is formed with a thickness of 50 nm (Figure 2d). With a deposition time longer than 250 s, the PB deposit thickness does not increase significantly.

In our case, the slow dissociation of ferricyanide

$$\mathrm{Fe(CN)_6}^{3-} + 6\mathrm{H}^+ \Leftrightarrow \mathrm{Fe}^{3+} + 6\mathrm{HCN}\uparrow \qquad (1)$$

must be the main source of ferric ions, needed for the formation of PB. UV/vis spectroscopic measurements of the ferricyanide solution showed that the characteristic absorption bands of ferricyanide at 302 and 421 nm decreased dramatically with the increase of the storage time of the acidic solution. In addition, no new absorption bands were observed, indicating no reduction of ferricyanide ion to ferrocyanide ion or other products. The driving force for the dissociation of ferricyanide must be the evolution of HCN gas (as shown in reaction 1) and the fast formation of PB. Further evidence of the influence of hydrogen ions on the dissociation rate of ferricyanide is supported by the slow formation rate of PB and the slight decrease in the UV/vis absorbance bands of ferricyanide in neutral solution.

The observed potential-dependent formation kinetics in the potential range from −0.5 V to EP demonstrate that the rate-determining step for the formation of PB is not the dissociation of ferricyanide ions. We suggest that the potential dependence is due to desorption of specifically adsorbed cyanide ions which block the active sites on the substrate for PB nucleation. Poskus et al. found that cyanide ions strongly adsorb on gold electrode surfaces, and the cyanide surface coverage decreases with a decrease of potential in the range from 0.25 to −1.5 V (SCE).[22] Therefore, a negative electrode potential is favorable for the nucleation and growth of PB. Since the desorption potential of cyanide ions at gold is more negative than EP, both the free ferric ions (reaction 1) and ferricyanide ions may be electrochemically reduced to ferrous and ferrocyanide ions. Reaction of these ions results in the formation of Prussian White (the reducted state of PB). In addition, the slow dissociation of the ferricyanide complex ensures a limited concentration of free ferric ions essential for the formation of compacted and defect-free ultrathin PB layer as in the case of the electroplating process.

Because of its exceptional uniformity and compactness, the ultrathin PB layer prepared by the present method shows a Nernstian potentiometric response (52 mV/decade) to potassium ions in a very broad concentration range (2.0 × 10^{-5} to 2.0 M) (Figure 3). Both a much broader response range for potassium ions as compared to that previously reported for PB or its analogue films prepared with other methods[12,23,24] and the easy preparation procedure as compared to that reported previously [4] (in which several tens of dip-coating steps are required to obtain good ion-selective performance) make the present ultrathin PB layer promising in the field of ion-selective electrodes. In addition, the ultrathin PB layer shows high catalytic activity and stability over a wide solution pH range (4 ≤ pH ≤ 8) toward the reduction of hydrogen peroxide that is an important intermediate of many biological reactions. For instance, the level of glucose in a biosystem can be monitored by the detection of hydrogen peroxide formed from an enzymatically catalyzed glucose oxidation. With the present PB ultrathin layer, a linear dependence of the cathodic current at −0.075 V on the concentration of hydrogen peroxide in a range of

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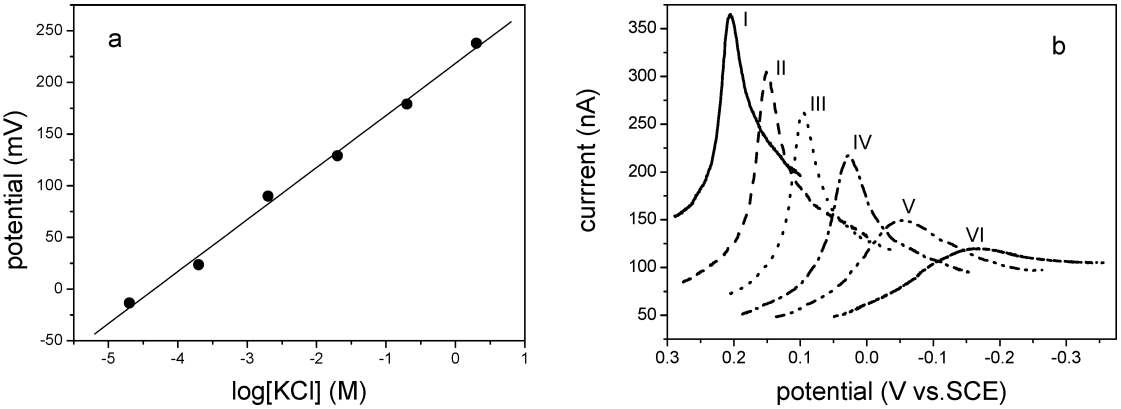

Figure 3. (a) Potentiometric Nernst response of an Au electrode previously deposited with a PB ultrathin film from an acidic ferricyanide solution of pH 1.6 and (b) the shift of the reduction potentials of an ultrathin PB layer modified Au for different concentrations of potassium ions. I, 2.0 M; II, 2.0 × 10^{-1} M; III, 2.0 × 10^{-2} M; IV, 2.0 × 10^{-3} M; V, 2.0 × 10^{-4} M; VI, 2.0 × 10^{-5} M.

$(2.0 \times 10^{-6})-(3.0 \times 10^{-2})$ mol/L can be obtained. The detection limit is 9.0×10^{-7} mol/L with a current response of 0.057 μA/cm^2. The high stability and wide detection range promise good performance in the field of biosensors.

In conclusion, we have developed a direct electrochemical approach for the formation of an ultrathin layer of PB nanoclusters with distinctive morphological properties from an acidic solution of ferricyanide. Our technique provides a simple and promising route for the local fabrication of molecular magnets, ion-selective sensors, and electro- or photochromics devices.

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Note Added after ASAP Posting

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