

Novel Method for Deposition of Gold–Prussian Blue Nanocomposite Films Induced by Electrochemically Formed Gold Nanoparticles: Characterization and Application to Electrocatalysis

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In this work, we report for the first time a one-step electrochemical deposition of gold–Prussian blue (PB) nanocomposite films. The catalytic activity of gold nuclei toward the decomposition of ferricyanide to free ferric ions and controlled generation of gold nanoparticles from HAuCl_4 solutions during potential cycling are exploited to form these nanocomposites. Concomitant electrochemical formation of both PB and gold phases leads to a “perfect blend”, in which each phase controls the growth of the other. The mechanism of formation and the features that distinguish this approach from others are highlighted. The nanocomposite films were characterized using voltammetry and UV–vis spectroscopy, field emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM). Interestingly, reversibility of the redox conversions of PB is enhanced by the presence of Au nanoparticles, as indicated by the reduced ΔE_p value in cyclic voltammetry and low charge-transfer resistance in *ac* impedance spectroscopy. The nanocomposite $(\text{Au-PB})_{\text{nano}}$ shows dramatically high catalytic activity toward electroreduction of hydrogen peroxide relative to that of PB on polycrystalline gold electrodes. Nanomolar detection of hydrogen peroxide is found to be feasible using these films at low cathodic potentials, which might be exploited to develop a new type of enzymeless biosensor.

Introduction

Among the transition metal hexacyanoferrates, Prussian blue (PB) or iron(III) hexacyanoferrate(II) is the classical prototype. Apart from their appealing solid-state chemistry and structural features, these compounds have gained recognition because of their electrocatalytic, electrochromic, ion-exchange, ion-sensing, and photomagnetic properties.^{1–5} The structural aspects and electrochemistry of PB have been previously reviewed in several articles, for example, in ref 6. As the transition between PB and its reduced form, Prussian white (PW) is associated with relatively faster electron-transfer kinetics and serves as the redox mediator in catalysis and electroanalysis.^{7,8} PB has been prepared by both chemical⁹ and electrochemical^{10,11} methods. If we confine ourselves to supported films of these compounds,

the most common strategy for electrosynthesis involves potentiodynamic cycling between preset potential limits of the working electrode in a supporting electrolyte containing both the metal ion (M^{n+} ; $\text{M} = \text{Fe}$) and ferricyanide species. Inert substrates such as glassy carbon (GC), graphite, platinum (Pt), or gold (Au) have been used. In these cases, the metal ions are added to the ferricyanide-containing supporting electrolyte. Potentiodynamic cycling then activates *in situ* precipitation of the insoluble PB on the inert substrate. A thin surface derivatizing layer of PB often imparts optimally fast electron-transfer characteristics to an underlying substrate. This electrocatalytic phenomenon is useful from both analytical (i.e., sensor) and electrosynthetic viewpoints. PB and its analogues have been considered as another class of interesting materials for electrocatalysis of reduction of hydrogen peroxide (H_2O_2), thus allowing its amperometric detection.¹² Among its redox states, the PW state has been recognized as reducing H_2O_2 and acting as an electron-transfer mediator between the electrode and H_2O_2 for its reduction to occur at low potentials. Monitoring of hydrogen peroxide content is of great importance in medicine, environmental control, and industry.¹³

Prussian blue has been extensively investigated in the form of thin polycrystalline electrodeposited films. It is now realized that the use of nanoparticles can improve the

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analytical performance for electroanalytical detection.¹⁴ Nanosized particles have unique physical and chemical properties, often showing very interesting attributes unmatched by their bulk counterparts. The large surface-to-volume ratio and the increased surface activity of nanoparticles, when compared to those of bulk materials, enable their use in catalysis and sensing. Nanoparticles of PB have been prepared using reaction conditions involving stabilization by PVP,¹⁵ synthesis in surfactant, and liquid crystalline media for magnetic^{16,17} and electrochemical applications.¹⁸ Karyakin et al.¹² have produced nanostructured thin films of PB for electrochemical applications, for example, in the detection of H₂O₂⁷ and glucose and in biosensors.¹⁹

In the context of generating nanostructures of PB, a few synthetic details need particular attention here: electrogeneration of PB films from solutions of hexacyanoferrate complexes has been extensively reported in literature.^{6,9} Gomathi and Rao²⁰ reported the formation of PB on glassy carbon (GC) electrodes when the anodic potential limit was extended to 1.5 V during potential cycling in ferricyanide + KCl solutions. Although potential excursion into high anodic potential region renders the interface acidic, favoring generation of ferric ions, high oxygen evolution in this potential region degrades the film quality. Yang et al.²¹ found that in a weakly acidic medium (pH 3.6), a thin film of PB is deposited on a gold electrode by using potential cycling. In an alternative electrochemical approach, an ultrathin layer of PB nanoclusters was observed²² to form on a gold electrode from an acidic solution of ferricyanide at potential negative with respect to the equilibrium potential of the ferric/ferrous redox couple. The slow decomposition ensures controlled supply of ferric ions needed for the formation of a compact ultrathin film of PB nanoclusters.

Eventhough PB formation can take place on Au from a single ferricyanide solution under low pH conditions,^{21–23} the growth was found to cease after a few number of cycles. In all these investigations, there is an implicit involvement of gold surface in the mechanism of ferricyanide decomposition, that may be corroborated by our present finding that glassy carbon surface does not favor this process as readily as Au. In addition, when ferricyanide solution is used in an acidic medium for potential cycling, the only solid phase that is formed on the electrode surface is PB, because the acid medium promotes release of ferric/ferrous ions that can combine with the solution ferricyanide. It is intriguing to ask *if another solid phase such as gold particles can be*

formed during this process. For this, a highly acidic species like hydrogen tetrachloroaurate needs to be present in the electrolyte medium. In what follows, we demonstrate that it is possible to arrive at a nanocomposite of particles of both PB and gold that electrocatalyzes reduction of hydrogen peroxide, leading to its nanomolar detection. In this novel approach, we take advantage of the interactions of HAuCl₄/Au and ferricyanide such as (a) Au-catalyzed decomposition of ferricyanide under low pH conditions for the supply of ferrous ions; (b) low interfacial pH arising from aqueous HAuCl₄ and (c) anodic oxidation of Au. In this environment, once Au is nucleated on GC, PB formation is instantaneous, a feature that distinguishes the present approach from those using sequential deposition, assembly on the basis of dendrimers,²⁴ and electrostatic layer-by-layer deposition.^{25,26} The formation process is elucidated and the resultant nanocomposite films are characterized using voltammetry UV–vis spectroscopy, FE-SEM, and AFM.

Experimental Section

HAuCl₄ (Aldrich) and potassium ferricyanide, potassium nitrate, hydrochloric acid, sulfuric acid, sodium hydroxide, and hydrogen peroxide from E-Merck were used as received. All aqueous solutions were prepared in Milli-Q water (18 MΩ, Millipore).

Voltammetric and amperometric experiments were carried out using a Potentiostat/Galvanostat BAS 100 B (Bioanalytical Systems Inc.) at ambient temperature (25 ± 1 °C). For voltammetric studies, a glassy carbon working electrode of area 0.07 cm² (BAS Inc.), a platinum foil auxiliary electrode, and an Ag/AgCl (3 M NaCl) reference electrode (BAS Inc.) were used; the potential values mentioned in this text are against this reference electrode. The surfaces of the glassy carbon and gold electrodes were polished using 4/0 grade alumina-coated emery paper. Prior to any electrochemical measurements, the electrode surfaces were examined for their cyclic voltammetric responses that are devoid of any redox peaks in the case of GC and characteristic gold dissolution/redeposition peaks in a potential range of 0.0 to 1.0 V. Alumina particles adhering to the electrode surface were removed by ultrasonication. Electrochemical impedance characteristics of the modified electrodes were measured using a Solartron system (Electrochemical Interface SI 1287 + Impedance/Gain-Phase analyzer SI 1260 coupled with a EG & G potentiostat model 273) in a frequency range of 0.1 MHz to 0.1 Hz at an impressed potential E_p , which is the midpeak potential of the redox peaks, $E_p = (E_{pa} + E_{pc})/2$ with an amplitude of 10 mV around E_p . Amperometric experiments were performed at a constant potential of 300 mV under stirred conditions with an addition of H₂O₂ at every 50 s time interval.

The UV–vis absorption spectra of the deposited films on fluorine-doped tin oxide (FTO)-coated glass substrates (supplied by Pilkington, USA, sheet resistance = 20 Ω/cm²) were collected on a Varian Cary-500 scan UV–vis–NIR spectrophotometer in the wavelength range of 200–800 nm. The FTO plates were cleaned by sonicating in detergent solution followed by treatment in an ethanol + water mixture. Au–PB nanocomposite films coated on

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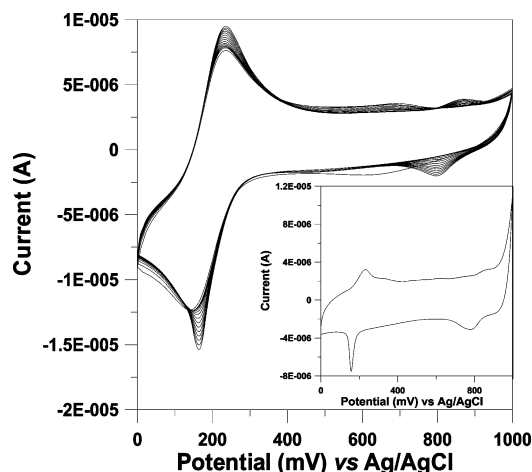


Figure 1. Cyclic voltammetric behavior of Au electrode during potential cycling in 0.1 M KNO_3 medium containing 1 mM potassium ferricyanide at pH 3.2 in the potential range from 0.0 to 1.0 V. Inset: Cyclic voltammogram of the PB-modified Au electrode in 0.1 M KNO_3 ; pH 3.2 (scan rate = 0.05 V s^{-1}).

FTO glass substrates were characterized using PicoSPM atomic force microscopy (Molecular Imaging) operated in contact mode. A gold-coated SiN_3 cantilever (Force Constant 0.12 N/m) was used as the force sensor and the radius of curvature of the probe tip was about $5\text{--}10 \text{ nm}$. The measurement was made with the “small” $6 \mu\text{m}$ piezoelectric z-scanner, which was standardized using calibration gratings. SEM measurements were made using Hitachi FE-SEM (Model S4700) with an acceleration voltage of 10 kV in normal mode.

Results and Discussion

Mechanism of Formation of PB on GC vis-à-vis Au.

Figure 1 shows the behavior of the polycrystalline (pc) Au electrode during potential cycling in KNO_3 medium containing potassium ferricyanide at pH 3.2 in the potential range from 1.0 to 0.0 V at $\nu = 0.05 \text{ V s}^{-1}$. After the electrode potential is cycled for more than 20 cycles, the surface of the Au electrode is modified with a small quantity ($1 \times 10^{-10} \text{ moles cm}^{-2}$) of PB as evident from the typical redox characteristics of PB as seen from the Figure 1 (inset). It is interesting to note that when the GC electrode on prolonged potential cycling in the medium using the above experimental conditions, no modification of the electrode surface with PB was observed. Recently, formation of PB on a gold electrode from acidic solutions containing single ferricyanide was reported by a few groups.^{21–23} The only paper where the formation of PB is described from single ferricyanide medium on GC is by Gomathi and Rao.²⁰ In this work, the authors employed extremely high anodic potential up to 1.5 V vs NCE to effect decomposition of ferricyanide/ferrocyanide ions in neutral KCl solutions that leads to the formation of PB on the electrode surface.

It is pertinent to know that PB formation on a glassy carbon surface has been reported to be a very slow process from solutions of low pH containing single ferricyanide. In the context of synthesizing a PB-based nanocomposite on the electrode surface, a gold-based acidic solution will be of great interest. One may believe that potential cycling of a gold electrode in acidic ferricyanide solutions can lead to the formation of this kind of nanocomposite, but the film

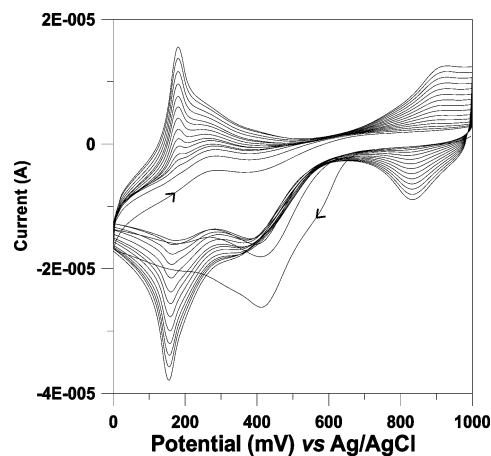


Figure 2. Cyclic voltammetric behavior of the GC electrode on potential cycling between 1.0 and 0.0 V in 0.1 M KNO_3 medium containing HAuCl_4 and potassium ferricyanide at scan rate = 0.05 V s^{-1} (measured solution pH 3.2).

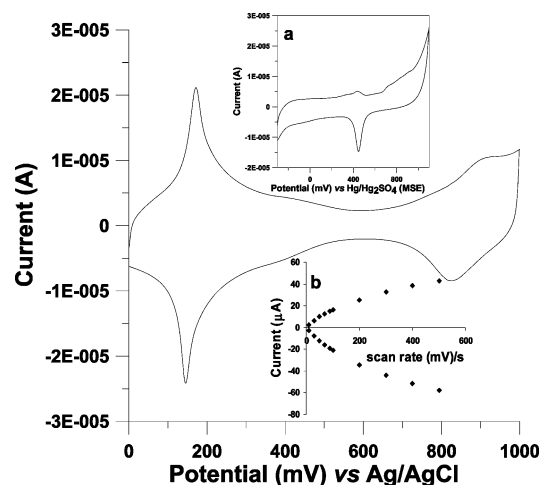


Figure 3. Voltammetric response of electrodeposited $(\text{Au-PB})_{\text{nano}}$ films on GC from a medium containing HAuCl_4 and potassium ferricyanide, in 0.1 M KNO_3 ; Inset: (a) CV response of the film in H_2SO_4 medium, after PB removal using alkali; (b) plot of peak current vs scan rate for anodic and cathodic peaks presented in figure.

formation is observed to cease after the formation of an extremely thin film (Figure 1). Obviously, continuous gold dissolution and redeposition needed for the nanocomposite formation is not possible in case of PB deposition on a polycrystalline gold electrode. Because PB formation on the electrode surface is basically an electrochemical process, acidic conditions combined with the presence of reducible gold ions in solution are likely to yield novel Au–PB nanocomposites. On the basis of this background, some of the observations on cycling the GC electrode between 0.0 and 1.0 V in medium containing 1 mM $\text{HAuCl}_4 + 1 \text{ mM}$ potassium ferricyanide in 0.1 M KNO_3 (Figure 2) assume importance. Interestingly, a continuous growth of voltammetric peaks during potential cycling (15 cycles), indicative of the formation of PB-like film on the GC electrode surface, was observed. The film-covered electrode was then shifted to a blank solution containing 0.1 M KNO_3 (acidified to pH 3.2) for cyclic voltammetric examination (Figure 3). The response observed is typical of Prussian blue in KNO_3 solutions and is free from features corresponding to that of Au. However, the features of Au appear when cycled in 0.1

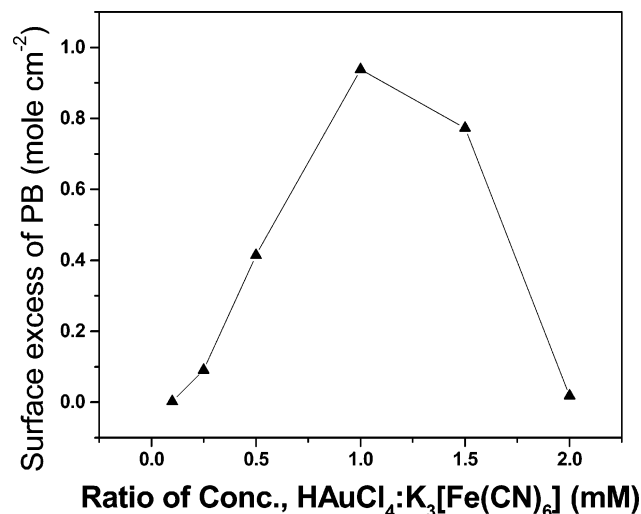


Figure 4. Variation of surface excess of (Au–PB)_{nano} composite on GC with [HAuCl₄]:[ferricyanide]; surface excess values calculated using the charge under the peak of PW scan rate = 0.05 V s⁻¹.

increased beyond 1 mM, the coverage of Au on GC is maximum and any further increase in its concentration results in the increased rate of deposition of gold more than necessary for PB formation.

After arriving at an optimum ratio of [AuCl₄⁻]:[ferricyanide] as 1:1 for the formation of (Au–PB)_{nano} composite, it is of interest to examine the role of solution pH vis-à-vis the interfacial pH. The pH of the solution employed for electrode modification was varied from 1.9 to 6.5. For the growth of the film, a solution of 0.1 M KNO₃ at different pH values containing equimolar (1 mM) potassium ferricyanide and HAuCl₄ was employed. The films deposited using 15 potential cycles between 1.0 and 0.0 V were examined for their cyclic voltammetric behavior in a blank solution of 0.1 M KNO₃ (see the Supporting Information, Figure S-1). It is evident from Figure S-1 that the formation of PB is limited in the very low pH region of 1.9 < pH < 3.2 and decreases when pH is increased beyond 3.2 to 4.5. It can be found from this figure that PB formation is maximum around pH 3.2. A further increase in pH to 6.5 does not show any PB formation. It is well-known that PB becomes unstable and ferricyanide dissociation is very slow in alkaline solutions.^{22b} It should be noted that the formation of PB from ferric chloride and ferricyanide by conventional electrochemical methods^{7,32} is favored at lower pH values. Although this is true in the case of PB deposition on GC electrodes, the low PB formation in the experiments involving HAuCl₄ and ferricyanide may be due to low electrodeposition of Au on GC at lower pH values because of the suppressed ionization of the gold complex (reaction 1). This observation also supports our argument that the electrodeposition of Au is a prerequisite for the PB formation. As the pH effect on ferricyanide dissociation to ferric ions is different from that of HAuCl₄ dissociation, it is not reasonable to assign the above behavior to the solution pH conditions. It is now confirmed that the deposition of PB is preceded by the generation and reoxidation of Au nanoparticles (eq 3) and the consequent changes in the interfacial pH. The solution pH also plays an important role in the sense that it controls the release of AuCl₄⁻ from the complex salt because of the

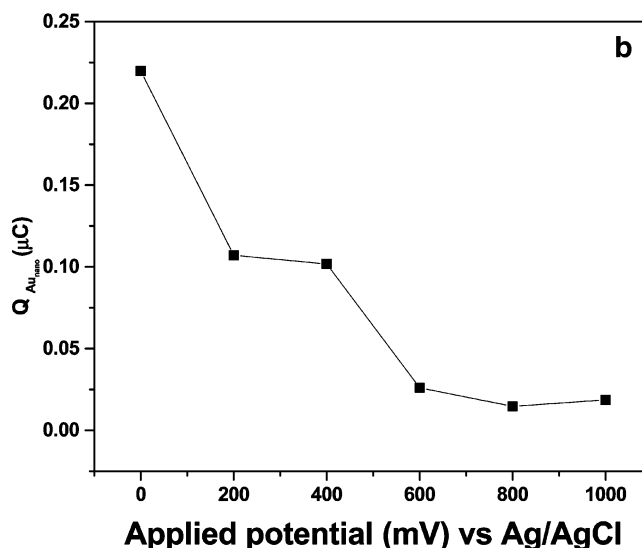
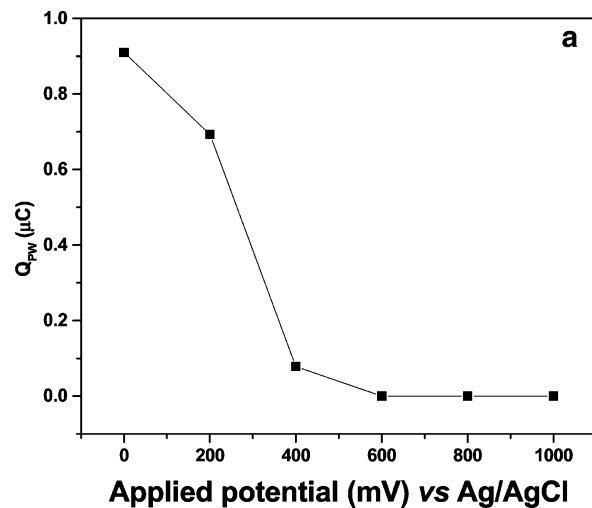


Figure 5. Effect of applied deposition potential on the charge under (a) Q_{PW} in 0.1 M KNO₃ (PW peak); (b) $Q_{Au_{nano}}$ in 0.1 M H₂SO₄ (reduction peak).

suppressed dissociation of the latter. In summary, it should be stressed that the interfacial/local pH conditions generated in eq 3 rather than the solution pH conditions are effective in the formation of PB.

Because the deposition of nanoparticles of both gold and PB are potential-dependent, studies on the effect of deposition potential on the formation of the nanocomposite are in order. The charge under the PW peak (Q_{PW}) as a function of applied potential under potentiostatic conditions was studied to elucidate the mechanism of PB deposition and its dependence on the presence of gold crystallites (clusters/particles) on the glassy carbon surface. Panels a and b in Figure 5 clearly show that PB deposition commences only after the gold crystallites are formed on the surface, as the applied potential should reach values cathodic to 0.4 V for the facile formation of the nanocomposite. This suggests that the nanocomposite formation can be elegantly controlled electrochemically. The deposition protocol is also amenable to improvements, as the control parameters such as potential pulse amplitude, [AuCl₄⁻]: [ferricyanide] and time can be varied at will.

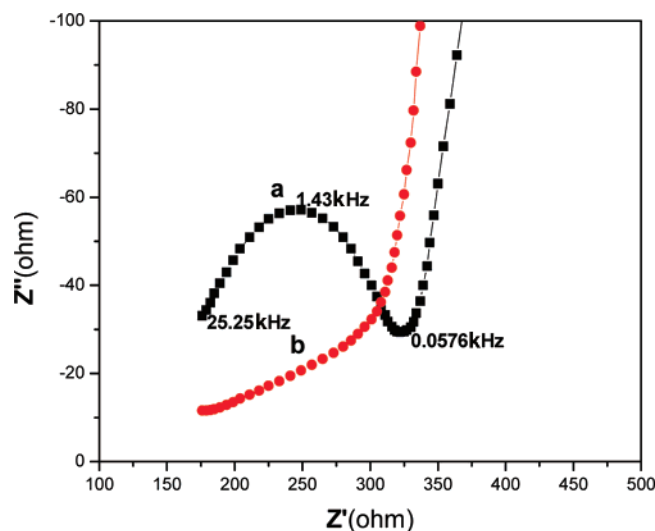


Figure 6. Nyquist plots of films of (a) PB formed on GC from ferric chloride and ferricyanide at pH 3.2 (black); (b) $(\text{Au-PB})_{\text{nano}}$ (red) at a bias potential corresponding to the midpeak potential $[(E_{\text{pc}} + E_{\text{pa}})/2]$ from Figure 3.

The nanocomposite films were routinely analyzed for their electrochemical response in blank solutions containing KNO_3 (pH 3.2), as the redox conversions of surface films of PB involve the ingress and egress of K^+ ions under cyclic voltammetric conditions. The symmetric voltammograms obtained at various scan rates exhibit current peaks with peak-to-peak separation (ΔE_{p}) of zero, and the peak current scales linearly with scan rate up to $\nu = 0.1 \text{ V s}^{-1}$, confirming the perfectly reversible surface redox process characteristics.³⁰ Though the redox transitions of conventionally prepared PB films are known to be highly reversible, most experiments thus far have shown deviation from an ideal ΔE_{p} by about 40–50 mV. It is interesting to find that our films of $(\text{Au-PB})_{\text{nano}}$ composite exhibit this ideal redox behavior. A plausible explanation that can be considered is the presence of gold particles in the nanocomposite that helps remove the resistive (iR) barriers in the film.

Electrochemical impedance characteristics were assessed to delve further into the redox characteristics of the film that show a distinct difference between the conventionally prepared PB and the $(\text{Au-PB})_{\text{nano}}$ composite films. Figure 6a presents a typical case in which the high-frequency region is marked by a semicircle that is associated with a finite charge-transfer resistance (R_{ct}) of approximately 200Ω , whereas in Figure 6b, the semicircle is a depressed one with reduced R_{ct} . This observation is in agreement with the results of cyclic voltammetric studies. The presence of incomplete Warburg part of the spectrum suggests that there is no significant diffusional barrier to charge transport within the films. The low-frequency region is capacitive in nature in both cases. The shift in the capacitive rise toward the high-frequency region for $(\text{Au-PB})_{\text{nano}}$ composite is an interesting feature that may reflect its enhanced switching characteristics. This highlights the role of PB-covered gold particles vis-à-vis unmodified gold particles in the film. The observation of near-zero ΔE_{p} and reduced R_{ct} implies an ideal mix in the nanocomposite and may prove valuable in devices involving fast switching rates.

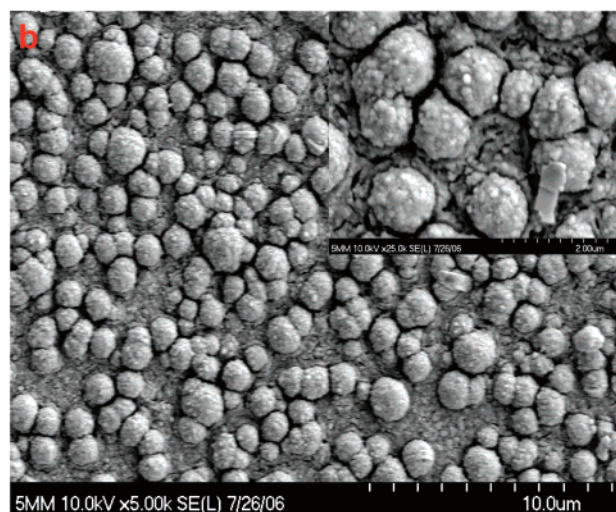
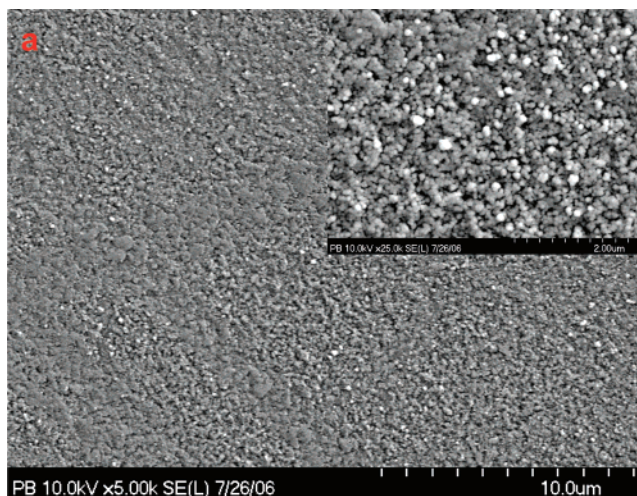
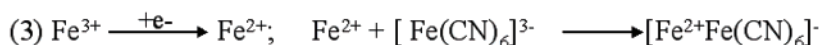
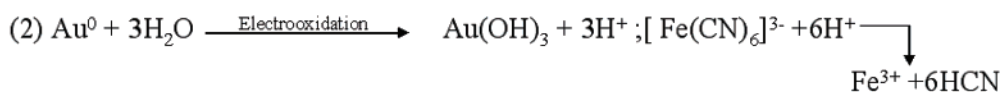
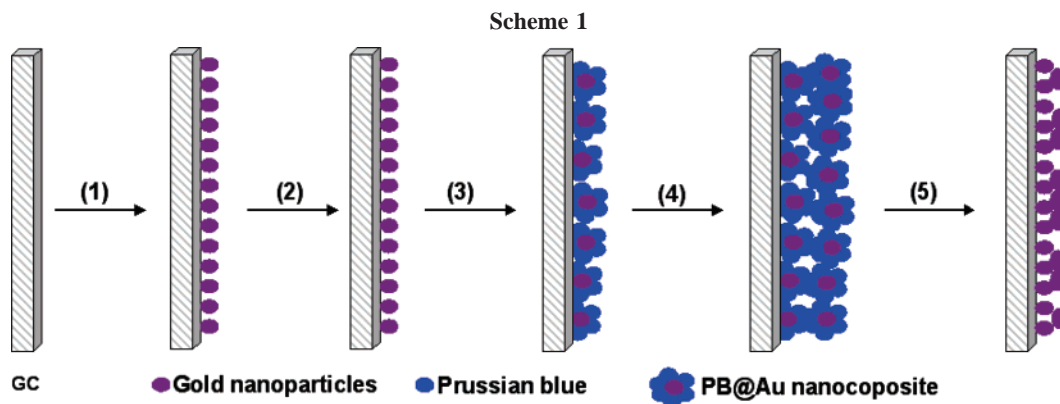


Figure 7. FE-SEM images of the films prepared on FTO glass substrates from solutions of (a) $\text{FeCl}_3 + \text{K}_3\text{Fe}(\text{CN})_6$ in 0.1 M KNO_3 ; (b) $\text{K}_3\text{Fe}(\text{CN})_6 + \text{HAuCl}_4$ in 0.1 M KNO_3 at pH 3.2. Inset: corresponding images at higher magnification.

To study the effect of thickness on the voltammetric behavior of the nanocomposite, we subjected GC to potential cycling for various cycle numbers (15–100 cycles) in the potential region mentioned above (see the Supporting Information, Figure S-1c). The ΔE_{p} obtained from the voltammetric responses presented in Figure S-1c does not deviate much from that expected for an ideal surface process, typically 10–15 mV. This confirms the film's perfectly reversible surface film characteristics. In a similar vein, no distinguishable semicircle associated with charge-transfer resistance was observed upon changing the thickness of the film. Detailed studies on the impedance characteristics of the nanocomposite as a function of thickness and gold content are under current investigation and will be reported separately.

Characterization of the Nanocomposite Film. The films were deposited by electrochemical cycling in a potential region of 0 to 1.0 V on cleaned FTO glass substrates for 15 cycles. The FE-SEM pictures show that (Figure 7a) the continuous film is composed of a closely spaced network of PB nanoparticles (20–50 nm in size) deposited from a mixture of ferric chloride and potassium ferricyanide, whereas spherically shaped $(\text{Au-PB})_{\text{nano}}$ composite ag-



(4) On continuous cycling between the potential region between 1.0 V to 0.0V

(5) Removal of PB in alkali

gregates 50–300 nm in size were observed for films formed using ferricyanide and HAuCl_4 (Figure 7b). It is believed that the gold nanoparticles being the “seeds” for the growth of PB are hidden inside of each aggregate. The presence of any unmodified exposed gold nanoparticles formed during gold deposition cycles is assumed to provide interaggregate contact within the film. It appears that the surface seeded with gold nanoparticles first favors the formation of PB over the nanoparticle surface as a nanocomposite film on continuous cycling. Although it appears that the method of preparation of nanocomposite is achieved with electrochemical cycling in a single step, more than one event take place, viz., PB formation preceded by gold nuclei formation, interdependent growth of each component of the nanocomposite. This sequence of events, as described in Scheme 1, leads to distinctly different morphological features. However, nanocomposite film composition and its dependence on the deposition conditions remain unexplored, and these aspects are of current interest in our laboratory.

The topological aspects of the film were analyzed using atomic force microscopy (see the Supporting Information, Figure S-2) that shows an approximate thickness of 100 nm with features corroborating the observations made in FE-SEM investigations. The larger aggregates contribute to the overall thickness of the film measured using AFM.

Because both gold nanoparticles and PB show absorption in the UV–vis region, the spectrum for the nanocomposite-modified FTO glass substrate was recorded in the region 300–800 nm. As can be seen from Figure 8, the absorption of PB starts from 400 nm to spread up to 800 nm with λ_{max} at 700 nm, in which the surface plasmon band corresponding to gold nanoparticles appears only as a shoulder at approximately 520 nm on the broad absorption of PB. The peak at 700 nm is due to the mixed-valence charge-transfer absorption of the polymeric Fe(II)–CN–Fe(III).³⁴ The

appearance of an absorption shoulder at 525 nm suggests that the composite film consists of gold nanoparticles deposited on the surface. This is in contrast with the observations of Qiu et al.,²⁶ where the surface plasmon resonance band at 525 nm is masked by the absorption of PB. These authors have attributed the absence of absorption at 520 nm to complete coverage of gold nanoparticles with Prussian blue. In the present case, the absorption around 520 nm can be due to either the “free” or “partially covered” gold nanoparticles. This feature might reflect the difference of the present method from that reported by Qiu et al. It is likely that the sequence of assembly employed by Qiu et al. ended with PB and an additional step of placing gold nanoparticles on the PB layer would have shown up as absorption maximum in the spectrum. The nanocomposites are usually amenable to theoretical treatments of Mie and Maxwell–Garnett,³⁵ but considering the lack of resolution

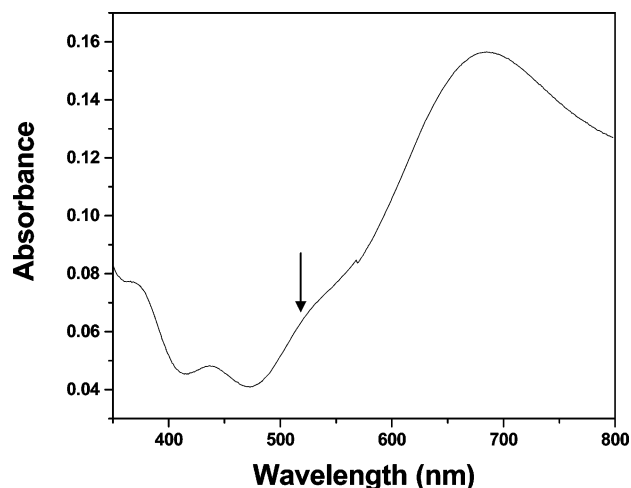


Figure 8. UV–vis absorption spectrum of $(\text{Au-PB})_{\text{nano}}$ film deposited on FTO glass substrate (arrow mark indicates surface plasmon absorption peak of Au_{nano}).

in the spectra observed in the present studies precludes such possibility with the existing data to elucidate the effect of the PB matrix on the surface plasmon band of gold nanoparticles. It is our intent to highlight this behavior in detail in a separate study.

Electrocatalytic Activity of (Au–PB)_{nano} for Electrocatalytic Reduction of Hydrogen Peroxide. Having established the conditions for the formation of the nanocomposite, it is worthwhile to consider these films for applications in electrocatalysis and electroanalytical chemistry. It is important to recognize the fact that PB electrocatalyzes reactions through redox mediation. Electrocatalysis through redox mediation needs, as a prerequisite, the catalyst to possess fast redox kinetics.³⁰ The potential at which the substrate reduction/oxidation takes place should be in proximity to that of the redox mediator. The role of gold nanoparticles is in providing a “platform” for the formation of nanostructured PB. One of the substrates that has attracted the attention of electrochemists in this context is the reduction of hydrogen peroxide, as its detection is of concern in analytical chemistry and biosensors.¹² The importance of nanocomposites in electroanalytical chemistry is obviously due to the inherently high surface-to-volume ratio and the consequent high signal-to-noise ratio that can aid detection at lower concentration levels with good sensitivity. Recently, we demonstrated signal enhancement in the detection of dopamine using the synergism between the polymer matrix and the gold nanoparticles, typically with sensitivity of $0.85 \mu\text{A nM}^{-1}$.³⁶ In this analytical approach, the gold particles enhance the current signal (sensitivity), whereas the polymer matrix aids separation of the current signals due to the analytes (selectivity). The impetus to undertake studies on the reduction of hydrogen peroxide and its detection was provided by the improved kinetics of redox of PB in the presence of gold nanoparticles, as the nanocomposite is characterized by near-zero ΔE_p and low R_{ct} (see Discussion). In addition, modifiers “perfectly blended” with a high-surface-area noble metal in the form of a nanocomposite are of current interest and expected to enhance the value of electroanalytical chemistry. In what follows, we show the superiority of these nanocomposite films in the nanomolar detection of hydrogen peroxide following its reduction.

Before describing the catalytic activity of the nanocomposite, a few remarks on the electrochemical properties of the PB films prepared through two different routes are appropriate here. Figure 9 presents the cyclic voltammograms of the films deposited (a) on a polycrystalline gold electrode by potential cycling in single ferricyanide solution (following the work in the literature^{21–23}) and (b) on a glassy carbon surface by potential cycling in a mixed solution of HAuCl_4 and potassium ferricyanide. It can clearly be seen that the current response is very poor in case (a), with a larger ΔE_p value compared to case (b). This may be understood in terms of the limited coverage of PB on a polycrystalline gold

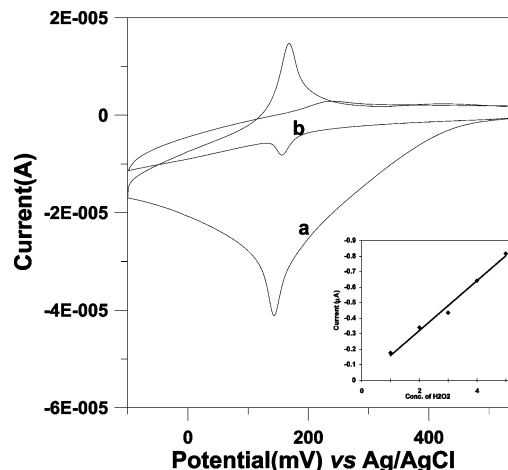


Figure 9. Cyclic voltammograms of (a) (Au–PB)_{nano} film; (b) PB on pc-Au; in presence of 1 mM H₂O₂ in 0.1 M KNO₃; pH 3.2, scan rate = 0.05 V s⁻¹. Inset: Plot of peak current vs concentration for (Au–PB)_{nano} film in a concentration range of 0–5 mM of H₂O₂.

surface;²² as the PB thickness increases, the surface is “starved” of gold concentration, whereas in case (b), as PB formation is dependent on the availability of gold particles on the GC surface generated by potential cycling, there is synchronized growth leading to the formation of a “perfect blend” of PB over gold and vice versa. In essence, the films produced in case (b) are associated with faster redox kinetics that qualifies to serve as a redox mediator. The highlight of this kind of nanocomposite films is that they exhibit an ideal surface-bound redox, unlike the films³⁰ that are associated with very high ΔE_p (typically, 210 mV), an indicator of the film’s capability to catalyze reactions through redox mediation. These results clearly demonstrate the ability to control the electrocatalytic characteristics of the nanocomposite at nanoscale. It is well-known that the glassy carbon surfaces are passive to hydrogen peroxide reduction and hence need to be chemically modified. GC electrodes modified with (Au–PB)_{nano} composite films were studied by cyclic voltammetry in blank 0.1 M KNO₃ (pH 3.2) and solutions containing 1 mM hydrogen peroxide (Figure 9a). For the sake of comparison, the response of the polycrystalline gold electrode modified with PB formed upon cycling in single ferricyanide solution (PB–Au_{pc}) is also presented in Figure 9b. The potential was cycled from 0.6 to –0.1 V vs Ag/AgCl in the blank and in the sample solution with a scan rate of 0.05 V s⁻¹ in both cases. These measurements were aimed at testing the catalytic activity of the nanocomposite film. As a first indication, the onset potential of hydrogen peroxide reduction on Au–PB nanocomposite is unmistakably less negative compared to that on PB–Au_{pc}. The catalytic current of hydrogen peroxide reduction at 0.30 V is related to the anodic current of the PB response. The catalytic effect per amount of catalyst can then be expressed as an activity factor, $\gamma = i_{(\text{Au-PB})\text{nano}}/i_{\text{PB-pc-Au}}$. For the determination of this factor, the same experimental conditions were employed for both electrodes. This factor works out to be approximately 3.8, as calculated using the peak current values from Figure 9. The current measurements performed for peroxide concentrations ranging from 0 to 5 mM show (see the Supporting Information, Figure S-3) an excellent linear relationship with the concentration (Figure 10, inset).

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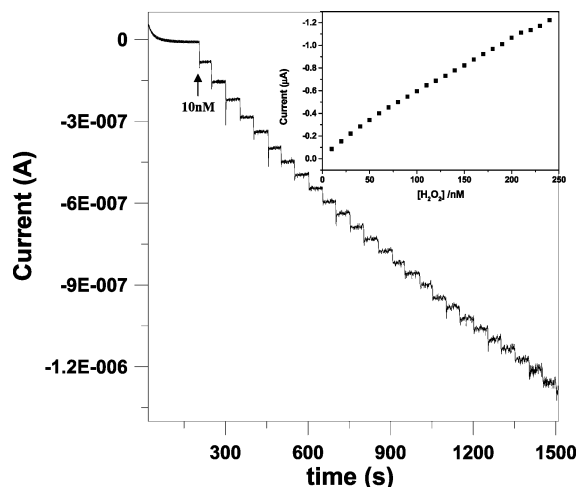
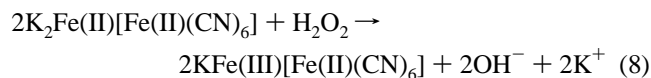


Figure 10. Amperometric detection of H_2O_2 using $(\text{Au-PB})_{\text{nano}}$ film in 0.1 M KNO_3 solution under stirring. Applied potential: 0.3 V. Inset: Plot of current vs $[\text{H}_2\text{O}_2]$ with each addition corresponding to 10 nM H_2O_2 .

Amperometry performed (as shown in Figure 10) using the nanocomposite at a working potential of 0.30 V yields a calibration plot (inset in Figure 10) for concentration in the nanomolar range (10 nM to 5 mM) with 5 nA/nM sensitivity and signal-to-noise ratio of 3. The response time of (<2 s) this sensor, usually estimated from the time required to reach 95% steady-state current, is much lower than those reported recently. The stability and renewability of the nanocomposite electrode are found to be very high, as the products of reduction of hydrogen peroxide do not affect the sensor performance in this range of concentration. A series of 10 measurements indicated good electrode-to-electrode reproducibility of the fabrication protocol described above. However, the nanocomposite appears to become unstable when used in high concentrations of hydrogen peroxide, possibly because of the generation of significant amounts of interfacial OH^- ions through the following mechanism^{37,38}



which damages the PB part of the nanocomposite. This

limitation is common to all PB-based H_2O_2 sensors but can be overcome in a flow-through cell arrangement, where the residence time is minimal. It is also possible to extend the application range of this kind of nanocomposites to electrochromic devices in order to increase the switching rates, and to biological sensors, for example, of the type reported in the literature.³⁹

Conclusions

A novel method based on Au-triggered electrochemical formation of PB from single ferricyanide is conveniently used for the synthesis of $(\text{Au-PB})_{\text{nano}}$ composite for electrode modification. The presence of gold nanoparticles not only enhances the reversibility of Prussian blue redox but also modifies the electrocatalytic activity of the nanocomposite film. This enhanced reversibility aids in catalyzing the reduction of H_2O_2 to occur at low potentials and enables amperometric detection at nanomolar levels. With gold nanoparticles and hexacyanometalate as a variant, there exist possibilities for enlarging the scope of these nanocomposites for various applications. This method offers several attractive features: first, the Prussian blue film is a relatively cheap and good electron-transfer mediator, which can enhance the current response and the sensitivity of the sensor; second, the electrodeposited gold nanoparticles present an excellent environmental and electrochemical stability. Using various experimental electrochemical parameters, it will be possible to control the growth of the composite at nanoscale levels. It is also expected that because of the interdependent growth of the nanocomposite, homogeneity of the films is built-in.

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Supporting Information Available: Figures S-1 through S-3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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