Palladium-Prussian blue nanoparticles; as homogeneous and heterogeneous electrocatalysts

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ABSTRACT

We report herein a synthetic strategy based on the use of tetrahydrofuran hydroperoxide (THF-HPO) that allows controlled conversion of palladium ion and potassium ferricyanide into palladium nanoparticles (PdNP) and water soluble Prussian blue nanoparticles (PBNP) respectively. The results revealed that THF-HPO provide a medium to enable the transformation of 3-aminopropyltrimethoxysilane (3-APTMS) capped palladium ions into PdNP of desired nanogeometry viz. $PdNP_1$ and $PdNP_2$. The processability of these two types of nanomaterials enabled the formation of PB-$PdNP_1$ and PB-$PdNP_2$ having potentiality for use either as homogeneous suspension or in heterogeneous matrix. The results based on peroxidase mimetic activity, cyclic voltammetry and amperometry revealed the gradual improvement in analytical performances of as synthesized nanomaterials as a function of palladium size and has been characterized by TEM, HRSEM and EDX analysis.

1. Introduction

Prussian blue (PB) and its analogues show attractive redox electrochemistry along with the electrochromic, electrochemically-induced ion exchange and electroanalytical properties [1–4]. Previous works have highlighted limitations of chemically synthesized PB due to restricted processability and nanogeometry available for practical applications [5–8]. For instance, PB-based modified electrodes for electrocatalytic reduction of H_2O_2 were limited to the use of electrosynthesized PB [9, 10]. Therefore, there has been challenging demand to synthesize PB for wider application in generating PB-based design with specific application to H_2O_2 sensing. One possible route is the synthesis of nano-sized PB which is likely to overcome such limitations due to dispersion ability of nanostructured material. Accordingly, an attempt on meeting such requirement has been made that allowed 3-aminopropyltrimethoxysilane (3-APTMS) and cyclohexanone mediated controlled conversion of potassium hexacynoferrate into Prussian blue nanoparticles (PBNP). As made PBNP displayed excellent nanogeometry, polycrystallinity and processability for use in both homogeneous as well as in heterogeneous systems [11] with impressive electron transfer rate constant to the order of $32\,s^{-1}$ as compared to that of many PB systems available in literature. Use of 3-APTMS during such controlled synthesis of superperoxidase mimetic polycrystalline PB and its analogues [12] may induce auto hydrolysis, condensation and

polycondensation reactions, affecting their bioanalytical applications. An alternative to 3-APTMS is the use of tetrahydrofuran-hydroperoxide (THF-HPO) as redox agent to synthesize processable PB [13]. The resulting PB nanomaterial responded well as both homogeneous and heterogeneous catalysts for H_2O_2 sensing, based on peroxidase mimetic electrocatalytic activities.

Still a need of electrocatalyst, comparable to that of natural systems like peroxidases, directed to facilitate nanocomposite formation combining PBNP to other nanomaterials such as metal nanoparticles. Organic reducing agents THF-HPO enable the formation of palladium nanoparticles (PdNP) of desired nanogeometry as a function 3-APTMS concentration [14]. In this work, we have thus examined the formation of nanocomposites of PBNP and PdNP of two differ size involving the participation of THF-HPO that enable homogeneous nanocomposite dispersion with possible synergistic effects of both PBNP and PdNP in electroanalytical applications since palladium nanoparticles has been one of known potential electrocatalyst. In addition, such nanodispersion has again been manipulated with two different sizes of palladium nanoparticles ($PdNP_1$ and $PdNP_2$) to yield three different systems: (i) PBNP alone, (ii) PB-$PdNP_1$ and (iii) PB-$PdNP_2$. Their catalytic properties were first investigated from aqueous suspensions (peroxidase mimetic activity and glucose detection) and then applied to the electrocatalytic sensing of hydrogen peroxide in both homogeneous and heterogeneous media.

Table 1
Comparison of different modified electrodes in the determination of hydrogen peroxide.

Substrate	Modifier	Operating potential/V	Linear range/µM	Sensitivity/µA mM^{-1} cm^{-2}	Detection limit/µM	Reference
GCE	PB-Fe$_2$O$_3$	−0.15	20–300	7.27[a]	11	[25]
CPE	FMCA-sol-gel-HRP	−0.10	Nr	30	nr	[26]
ITO	[PAH/PB@Au]$_n$	−0.10	0.1–100	Nr	nr	[27]
GCE	PB/POPD	−0.05	0.1–120	2800	0.05	[28]
GCE	PBNPs/Nafion	−0.05	10–6000	138.6	1	[29]
GCE	CR-GO	−0.20	2.1–140	Nr	0.05	[30]
Pt	SAPB	−0.05	1–400	625	nr	[31]
CPE	Sol-gel-ferrocene/HRP/sol-gel	0	3–57	67[a]	0.6	[32]
CPE	PB-AuNP$_2$-Pd$_2$	0	50–1000	323.10	0.1	[5]
CPE	PBNPs	0	0.5–1000	108.8	0.2	This work
CPE	PB-PdNP$_1$	0	0.2–1000	221.6	0.1	This work
CPE	PB-PdNP$_2$	0	0.1–1000	374.1	0.1	This work

[a] µA mM^{-1}; nr = not reported; GCE = glassy carbon electrode; CPE = carbon paste electrode; PAH = poly(allylamine hydrochloride) AuNP = gold nanoparticles; CR-GO = chemically reduced graphene oxide; ITO = indium tin oxide; PBNP = Prussian blue nanoparticles.
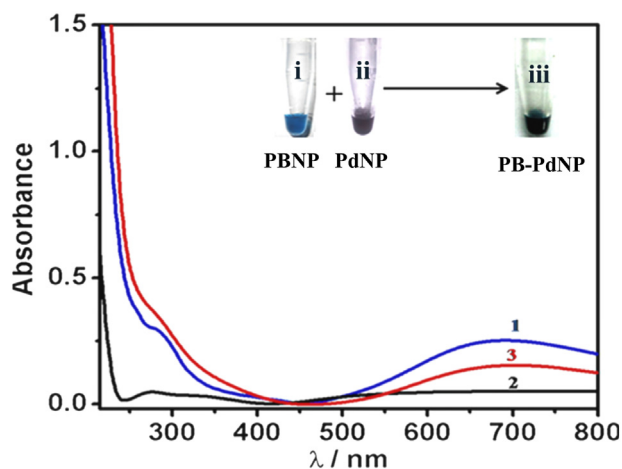

Fig. 1. Absorption spectra of PBNP (i), PdNP$_1$(ii), and PB-PdNP$_1$ (iii).

2. Experimental detail

2.1. Materials

Graphite powder (particle size = 1–2 µm), Nujol oil (density- 0.838 g mL^{-1}), and 3-Aminopropyltrimethylsilane (3-APTMS) were obtained from Sigma-Aldrich Co., India. Potassium ferricyanide, hydrogen peroxide and tetrahydrofuran (THF) were purchased from Merck, India. Tetrahydrofuran-hydroperoxide (THF-HPO) was synthesized by autoxidation of THF. Potassium tetrachloropalladate was purchased from HiMedia, India. All other chemicals used were of analytical grade. The water used in experiments was double distilled–deionized water (Alga water purification system).

2.2. Electrochemical measurements

All electrochemical measurements were performed on Electrochemical Workstation Model CHI660B, CH Instruments Inc., TX, USA in an electrochemical cell equipped with a three electrode having CPE-PBNP/CPE-PB-PdNP$_1$/CPE-PB-PdNP$_2$ as working electrode, platinum and Ag/AgCl as counter and reference electrode respectively in a working volume of 3 mL. The cyclic voltammogram measurements were performed in 0.1 M phosphate buffer pH -7.0. The amperometric measurement were at 0.0 V vs Ag/AgCl for the electrochemical reduction of H$_2$O$_2$ whereas at 0.6 V vs Ag/AgCl for the oxidation of the H$_2$O$_2$ (generated as a function of glucose oxidase catalyzed reaction) in 0.1 M phosphate buffer solution (pH -7.0) containing 0.5 M KCl at 25 °C. The active electrode surface areas were determined by electrochemical measurements as reported earlier [15, 16].

2.3. Characterization and kinetic assay

The absorption spectra of nanoparticles and kinetic measurements were recorded using Hitachi U-2900 spectrophotometer. Transmission electron microscopy (TEM) was conducted with Morgagni 268D (Fei Electron Optics) transmission electron microscope operating at 200 kV. The steady state kinetics associated to the peroxidase mimetic activity was investigated by varying the concentration of H$_2$O$_2$ (0–25 mM) at a fixed concentration of o-dianisidine (50 µM). The reaction was carried out in 2 mL phosphate buffer (0.1 M, pH -7.0). The variation of absorbance was monitored in time scan mode at 430 nm (ε = 11.3 mM^{-1} cm^{-1}). The kinetic parameters were calculated by fitting the absorbance data to the Michaelis-Menton equation.

2.4. Glucose detection using glucose oxidase as homogeneous catalysts

The analysis was performed as follows: (a) 40 µL of 10 mg mL^{-1} Glucose oxidase and 200 µL of glucose at different concentrations in 0.1 M phosphate buffer (pH~7.0) were incubated at 35 °C for 45 min; (b) 50 µL of o-dianisidine (0.5 mM), 15 µL of PB-PdNP$_2$ and 1695 µL of 0.1 M phosphate buffer (pH~7.0) were added to the above reaction solution; (c) the reaction mixture was incubated at 45 °C for 30 min followed by measurement of absorption at 430 nm.

2.5. Synthesis of PBNP and its nanodispersion with PdNP

In a typical procedure 50 µL aqueous solution of potassium ferricyanide (0.5 M) was mixed with 200 µL of tetrahydrofuran hydroperoxide (THF-HPO) under stirred conditions over a vertex cyclomixer. The mixture immediately turns into green colour which was left to stand for 12 h. The colour of the solution turned to blue indicating the formation of PBNP. As synthesized PBNP was treated with ethyl acetate to eliminate residual organic moiety and collected by centrifugation followed by washing and drying.

In a typical procedure, PdNP were synthesized by mixing an aqueous solution of K$_2$PdCl$_4$ (0.003 M, 50 µL) and 10 µL of two different concentrations of 3-APTMS i.e. 0.5 M and 1 M under stirred condition over a cyclo mixer followed by the addition of THF-HPO (15 µL) in each one at room temperature resulting the formation of PdNP$_1$ and PdNP$_2$ respectively. The mixture turns into light black colour within < 15 min which subsequently converted to dark black colour of PdNP sol of different size i.e. PdNP$_1$ and PdNP$_2$ as a function of 3-APTMS concentrations (0.5 M, 1 M). The nanocomposite formation involves the mixing of 100 µL of PBNP and 50 µL of PdNP$_1$ or PdNP$_2$ solutions, leading to the formation of a homogeneous nanodispersion of PB-PdNP$_1$ and PB-