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Pt nanoparticle-based highly sensitive platform for the enzyme-free amperometric sensing of H_2O_2

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ABSTRACT

Highly sensitive electrochemical platform based on polymer supported Pt nanoparticles (nPts) for the amperometric sensing of H_2O_2 at sub-nanomolar level without any redox mediator or enzyme is developed. The nPts are generated by the chemical reduction of precursor pre-organized on the electrode surface and characterized by field emission scanning electron microscopy, X-ray diffraction, spectral and electrochemical measurements. The cationic polymer poly(diallyldimethylammonium) chloride was used to assist the pre-organization of metal precursor. nPts on the electrode surface have an average size of 17 nm. The nanoparticles show excellent electrocatalytic activity towards oxidation of H_2O_2 at less positive potential than the polycrystalline Pt electrode. Unlike the polycrystalline Pt electrode, the nanoparticle-based electrode does not undergo deactivation by surface oxides and other species in solution. Particle loading on the electrode surface controls the electrocatalytic activity. The nanoparticle-based electrode is highly sensitive (9.15 μA/mM) and display linear response up to 3 mM. It could detect 0.5 nM (S/N = 5) of H_2O_2 under hydrodynamic condition in neutral solution and the electrode is highly stable. The detection limit achieved is significantly lower than the other nanoparticle-based electrodes. The excellent performance of the electrode is ascribed to the good catalytic activity of the particle and ensemble behavior of the nanoparticle-modified electrode. The analytical performance of the electrode in the development of glucose biosensor is demonstrated. The biosensor is used for the sensing of glucose in the micromolar level in neutral pH.

1. Introduction

Development of reliable analytical methodology for the precise monitoring of H_2O_2 is of significant interest in the fabrication of biosensing devices, environmental control and industries. H_2O_2 is recognized as a strong oxidant in the conversion of dissolved SO_2 to H_2SO_4, which is the main contributor to the acidification of aqueous phase of the troposphere (Brandt and Eldik, 1995; Calvert et al., 1985). Moreover, H_2O_2 is a product of the reaction catalyzed by large number of oxidase enzymes. The diagnostic response of many biosensing devices is based on the measurement of enzymatically generated H_2O_2 (Turner et al., 1987). Furthermore, H_2O_2 is the most valuable marker for oxidative stress and it is a precursor in the formation of highly reactive and potentially harmful hydroxyl radical (Yorek, 2003; Theruvathu et al., 2001). Various analytical methods including spectral, electrochemical, etc. have been used for the sensing of H_2O_2 (Evans et al., 2002; Liu et al., 2005; Mao et al., 2002; Lin et al., 2007; Polsky et al., 2006). The electrochemical methods are preferred because of high sensitivity, fast response and it requires low-cost equipments. H_2O_2 can be detected electrochemically either by its reduction or oxidation. Detection of H_2O_2 by its oxidation has many advantages, as the interference from oxygen can be avoided. The electrochemical detection of H_2O_2 requires highly sensitive and selective transducer. The carbon paste, carbon nanotube, mediator and peroxidase-based electrodes have been used for the sensing of H_2O_2 (Wang et al., 1992; Ruzgas et al., 1996; Karyakin et al., 2004, 2007). The major problem associated with the mediator-modified electrodes is the lack of long-term stability due to the leaching of mediator from the electrode surface. Pt-based electrodes have been traditionally used for the detection of H_2O_2. However, deactivation of electrode surface due to the formation of surface oxide is one of the problems associated with Pt electrodes (You et al., 2003). The voltammetric response of H_2O_2 on Pt electrode is further complicated by the competitive adsorption of dioxygen on the electrode surface and the protonation of adsorbed H_2O_2 complex (Hall et al., 1998). Pt-black, Pt-black microarray and mesoporous Pt electrodes have been used to achieve high sensitivity towards H_2O_2 (Kicela and Daniele, 2006; Sandison et al., 2002; Evans et al., 2002). Recently, Pt nanoparticle-based electrodes have been employed for the sensing of H_2O_2 (You et al., 2003; Hrapovic et al., 2004; Male et al., 2007; Yang et al., 2006; Karam and Halaoui, 2008).

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Utilization of microelectrode array or nanoelectrode ensemble is one of the fascinating approaches in the field of electroanalytical chemistry to achieve high sensitivity and low detection limit. The use of such electrodes for the electroanalysis of bioanalytes has several advantages over the conventional macroelectrodes. In principle, the electroanalytical detection limit at micro/nanoelectrode ensembles is expected to be much lower than that of a macrosized electrode of analogous area due to the enhancement in the signal-to-noise (S/N) ratio (Reller et al., 1984; Penner and Martin, 1987; Wehmeyer et al., 1985; Cheng et al., 2002; Demaille et al., 1997). Bard and co-workers for the first time used the colloidal chemical approach for the development of ensemble (Demaille et al., 1997). Recently, Dong and co-workers have successfully demonstrated the seed mediated growth approach for the development of ensemble of nanoparticles (Cheng et al., 2002).

Transition metal nanoparticles have attracted considerable interest in the development of electrochemical sensors and biosensors owing to their extraordinary catalytic activity (Katz et al., 2004; Privett et al., 2008; Mao et al., 2003; Zhang et al., 2004; Gong et al., 2007). The large surface-to-volume ratio and special binding site on the surface of nanoparticles make them an efficient catalyst in various reactions. It is promising to develop electrochemical interface based on arrays/ensembles of metal nanoparticle for sensing applications, as such interface is expected to be highly sensitive. In the present investigation, we describe a simple approach for the development of a highly sensitive electrochemical interface and its analytical application in the amperometric sensing of H_2O_2 and glucose. The electrochemical-sensing interface has been developed by the pre-organization of metal precursors on a polymer-modified conducting substrate and subsequent chemical reduction of the precursor to nanosized metal. The nanoparticle-based platform displays excellent performance in terms of operating potential, detection limit, stability and reproducibility with respect to the existing nanoparticle based and polycrystalline Pt electrodes.

2. Experimental

2.1. Materials

Poly(diallyldimethylammonium) chloride (PDDA) and H_2PtCl_6 were obtained from Sigma–Aldrich. Analytical grade hydrogen peroxide was obtained from Merck. All other chemicals used in this investigation were of analytical grade. All solutions were prepared using Millipore water (18 MΩ cm). Glucose oxidase (GOD) (125 U/mg, from *Aspergillus niger*) was obtained from Sigma–Aldrich.

2.2. Instrumentation

Electrochemical measurements were performed using a divided cell in three-electrode geometry with a glassy carbon working electrode, a Pt wire auxiliary electrode and Ag/AgCl (3 M KCl) reference electrode (BAS). Cyclic voltammograms were recorded using model 842B electrochemical analyzer (CH Instruments, Austin, TX) attached to a picoamp booster-Faraday cage. All the potentials are measured with respect to Ag/AgCl reference electrode. JEOL JEM 6700F field emission scanning electron microscope (FESEM) was used to obtain FESEM images of the nPt dispersed on the PDDA. X-ray diffraction analysis of the nanoparticles was carried out with a Phillips Holland X'Pert PRO X-ray diffraction unit. Absorption spectral measurements were made with Mikropack UV-VIS-NIR, DH 2000.

2.3. Procedure

The nPts were obtained by the chemical reduction of $PtCl_6^{2-}$, which was pre-organized on the electrode modified with PDDA according to Scheme 1. Typically a cleaned glassy carbon electrode (GCE) was first modified with PDDA by casting 10 μL of 0.5% (v/v) aqueous PDDA and dried at room temperature for 30 min. Then the modified GCE was soaked in an aqueous solution of 0.25% (w/v) $PtCl_6^{2-}$ for required time (1–5 min) for the pre-organization of metal precursor on GCE surface. The cationic polymer on GCE assists the pre-organization of metal precursor by electrostatic interaction. This metal precursor pre-organized GCE was then soaked in 0.08% (w/v) aqueous solution of $NaBH_4$ for 30 min for the reduction of the pre-organized metal precursor to metallic Pt. Then the electrode was washed with copious amount of water and phosphate buffer solution and subjected to electrochemical experiments. For FESEM, UV–vis spectral and XRD measurements, microscopic glass slides were used instead of GCE.

3. Results and discussion

3.1. Characterization of nPt on the electrode surface

The UV–vis spectrum of $PtCl_6^{2-}$ in aqueous solution shows an absorption band at ~260 nm (Supporting information) due to the ligand-to-metal charge transfer (Creighton and Eadon, 1991). However, the pre-organized $PtCl_6^{2-}$ displays an absorption band at ~319 nm. The shift in the absorption band is ascribed to complexation of $PtCl_6^{2-}$ with the N atom of PDDA. The complexation of $PtCl_6^{2-}$ with positively charged polymer is known to shift the absorption band to higher wavelength side (Jiang et al., 2006). The band observed at 319 nm became structureless after the reduction of the precursor (Supporting information). Fig. 1 is the FESEM image obtained for the nPts on the microscopic slide. The spherical nanoparticles have an average size of 17 nm. The nanoparticles are randomly distributed and the interparticle distance (10–30 nm) is not uniform. Although the nanoparticles do not have uniform size and shape, they are distributed throughout the surface and it can be considered as nanoparticle ensembles. Such feature was not observed for bare PDDA-modified electrode (Supporting information). The XRD pattern obtained for nPts shows three distinct peaks corresponding to (1 1 1), (2 0 0) and (2 2 0) planes. The ratio of the intensity of (1 1 1) plane to the (2 0 0) plane is significantly higher than the conventional value, indicating that the nPt has predominant (1 1 1) plane (Supporting information). The crystallite size was calculated from X-ray line broadening analysis using

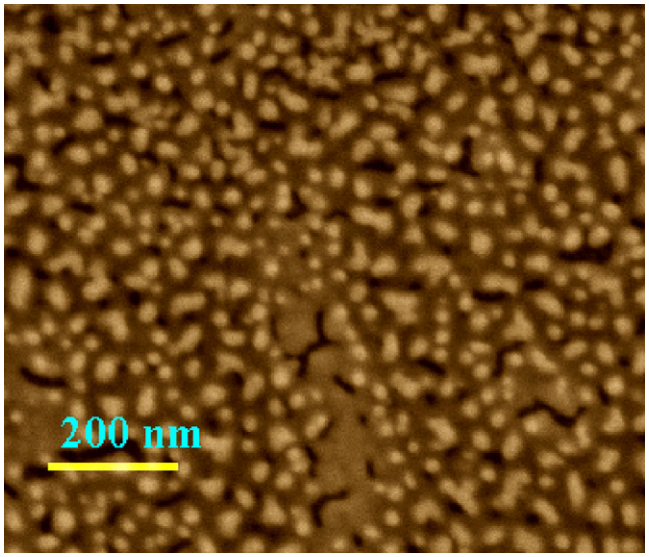
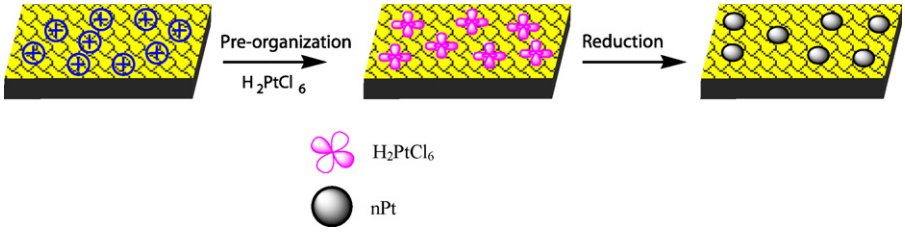


Fig. 1. FESEM image obtained for nPts on the PDDA-modified surface.



Scheme 1. Scheme illustrating the pre-organization of H_2PtCl_6 and generation of nPts.

the Scherer formula (Cuilty, 1978) and is in close agreement with the average size obtained from FESEM data. The EDS measurement further confirms the existence of nPts (Supporting information).

The nanoparticle-modified electrode displays typical voltammetric response characteristics of metallic Pt in 0.1 M H_2SO_4 (Supporting information). The electrochemically accessible area (real surface area) of nPts on the electrode surface was determined from the charge consumed during the hydrogen adsorption/desorption (Supporting information) and was 0.432 cm^2 (obtained at 5 min pre-organization time). The loading of nPts on the electrode surface was controlled by changing the pre-organization time of metal precursor. Increase in the pre-organization time lead to an increase in the amount of precursor on the electrode surface. As anticipated, a steady increase in the surface area of electrochemically accessible nPts was observed up to the pre-organization time of 5 min (Supporting information). Further increase in the pre-organization time does not have significant effect in the surface area.

3.2. Electrocatalysis

Fig. 2 illustrates the electrocatalytic effect of nPts towards oxidation of H_2O_2 in phosphate buffer solution (PBS) at neutral pH. Well-defined voltammogram for the oxidation of H_2O_2 was obtained (Fig. 2A); the oxidation peak appears at ~0.4 V at the scan rate of 10 mV/s at lower concentration and it slightly shifts to positive potentials while increasing the concentration of H_2O_2. The oxidation peak current linearly scales with the square root of scan rate, suggesting diffusion controlled process. In the case of polycrystalline Pt electrode, oxidation of H_2O_2 occurs at more positive potential (>0.5 V) and the voltammogram is rather broad (Supporting information), presumably due to the sluggish electron transfer kinetics. The voltammetric response on the polycrystalline Pt is not reproducible; gradual decrease in the current and shift in the peak potential were noticed during subsequent sweeps. Significant decrease in the overpotential and remarkable increase in the peak current obtained on the nanoparticle-modified electrode indicates the excellent electrocatalytic activity of nPts on the electrode surface. The electrocatalytic response on the nanoparticle-modified electrode was very stable; the peak potential and peak current did not change upon repeated sweeps. As shown in Fig. 2 gradual increase in the peak current while increasing the concentration of H_2O_2 was obtained and the calibration plot is linear up to 3 mM. The sensitivity of the electrode was calculated from the calibration plot and was 9.15 μA/mM.

It is worth noting that the electrocatalytic activity of nPts depends on amount of nPts loaded on GCE surface. As described earlier, the loading of nPt on the electrode surface was controlled by changing the pre-organization time. Negative shift in the oxidation peak potential and increase in the peak current were obtained while increasing the loading of nPt on the electrode surface (Supporting information). Maximum electrocatalytic current for the oxidation of H_2O_2 was obtained with the electrode prepared at 5 min pre-organization time. Further increase in the loading did not influence the catalytic current. The negative shift in the peak potential clearly indicates that the particle loading has tremendous effect on the electron transfer kinetics. The presence of nanoparticles on the electrode surface facilitates the electron transfer. These results are in accordance with the existing literature on ensembles of nanoparticle (Kumar and Zou, 2005, 2009). It has been shown that electrooxidation of CO strongly depends on the coverage of particles on the electrode surface (Kumar and Zou, 2005). Negative shift in the peak potential and increase in the peak current have been

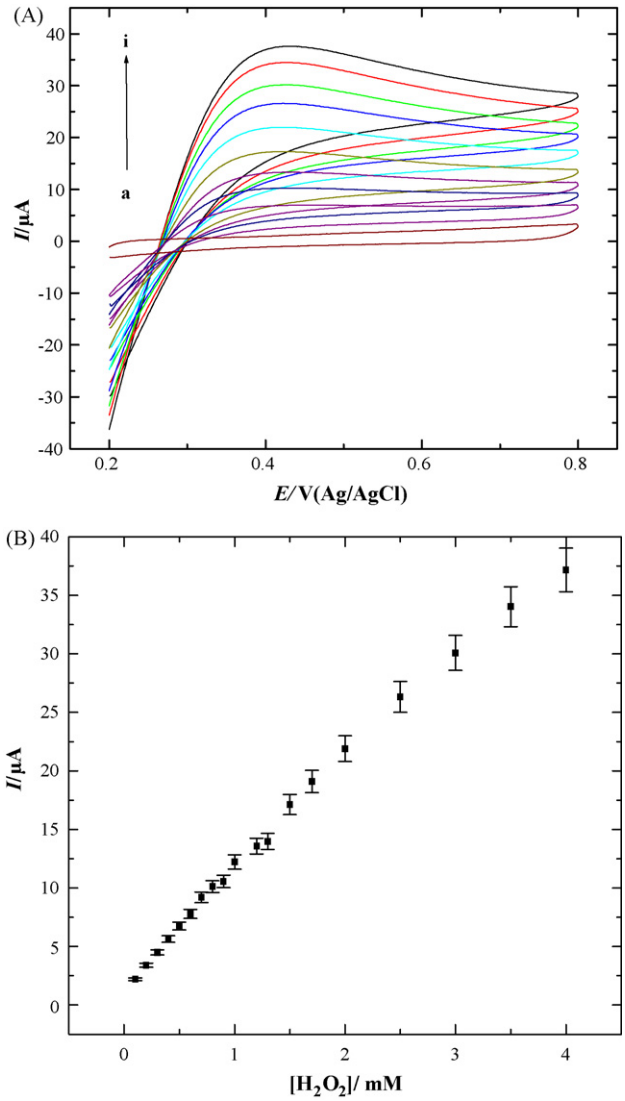


Fig. 2. (A) Cyclic voltammograms illustrating the electrocatalytic effect of nPts towards oxidation of H_2O_2 in PBS (pH 7.2). Scan rate: 10 mV/s, [H_2O_2] (a) 0.5 mM, (b) 0.8 mM, (c) 1.2 mM, (d) 1.5 mM, (e) 2 mM, (f) 2.5 mM, (g) 3 mM, (h) 3.5 mM and (i) 4 mM. Voltammograms obtained at lower concentrations are not shown for clarity reason. (B) Calibration plot obtained for all concentrations. Current measured at the potential of 0.4 V was plotted against concentration of H_2O_2.

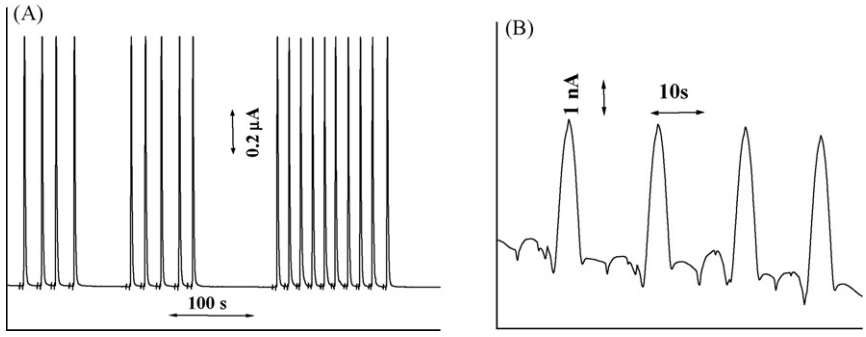


Fig. 3. (A) Flow injection amperometric response of the nanoparticle-modified electrode towards H_2O_2. Twenty microliters of 10 μM H_2O_2 was injected at regular interval. (B) Response obtained for the injection of 0.5 nM H_2O_2. Electrode potential: 0.5 V. Mobile phase: PBS of pH 7.2. Flow rate: 1 mL/min.

observed while increasing the particle coverage on the electrode surface and it has been explained by considering the nanoparticle electrode as an ensemble electrode (Kumar and Zou, 2005). In the present case, it is believed that nPts on the electrode surface behaves like ensemble of nanoelectrodes. The negative shift in the peak potential and enhancement in the peak current is attributed to the ensemble behavior of the electrode and the high catalytic activity of the nanoparticles. As can be seen from Fig. 1, the nanoparticles are randomly distributed throughout the surface. Such surface can be considered as nanoparticle ensembles. The voltammetric profile of an analyte on an ensemble electrode is determined by the sweep rate and the interparticle distance (Reller et al., 1984; Penner and Martin, 1987; Wehmeyer et al., 1985; Cheng et al., 2002; Demaille et al., 1997). In the case of total overlap regime, the analyte would show peak shape voltammogram, as the diffusion layers at the individual particle overlap to produce diffusion layer which is linear to the entire geometrical surface area of the electrode (Reller et al., 1984; Penner and Martin, 1987; Wehmeyer et al., 1985; Cheng et al., 2002; Demaille et al., 1997). In our case, we observed peak shaped voltammogram and is due to the total overlap of the diffusion layer at the individual particles on the electrode surface. The negative shift in the peak potential can be ascribed to the change in the diffusion pattern (Kumar and Zou, 2005). The diffusion pattern changes from mixed nonlinear and linear to linear while increasing the particle loading on the electrode surface (Kumar and Zou, 2005).

3.3. Flow injection amperometric sensing of H_2O_2

The analytical performance of the electrode was examined with amperometric flow injection analysis. Fig. 3 shows the flow injection response obtained for H_2O_2. The electrode potential was held at 0.5 V and 20 μL of H_2O_2 (10 μM) was injected at regular intervals. Very reproducible response was obtained upon repeated injection of H_2O_2 (Fig. 3), confirming that the electrode does not undergo deactivation during the experiments. The nanoparticle-modified electrode could detect as low as 0.5 nM (S/N = 5) of H_2O_2 without any additional redox mediator or enzyme being necessary (Fig. 3 inset). This nanoparticle-based electrode is excellent in performance compared to the existing Pt nanoparticle-based electrodes (Table 1). As summarized in Table 1, the limit of detection achieved with the present electrode is significantly lower than those of the other Pt nanoparticle-based electrodes. An added advantage of the present electrode is that the detection potential is 50–100 mV less positive than those of the other electrodes. Lyon and Stevenson reported the detection limit in the picomolar level using chemically activated redox mediator in solution (Lyon and Stevenson, 2006). However, this method requires diffusional redox mediator and enzyme horseradish peroxidase. The disadvantage of this method is that the redox mediator easily adsorbs on the electrode surface and hence deactivation of the electrode is inevitable. In the present investigation, our nanoparticle-modified electrode could detect H_2O_2 in the sub-nanomolar level under hydrodynamic condition without any enzyme or redox mediator and shows linear response up to 4 mM. The nanoparticle-modified electrode is highly stable and it does not undergo deactivation upon repeated use. As can be seen from Fig. 3, the amperometric response in the flow injection experiment is reproducible over time. The stability was further tested by using the same electrode for 1-week time. The amperometric response of the electrode towards H_2O_2 was made for 1 week. The electrode was stored in PBS after the measurement during the week. The amperometric current was stable for 5 days and 22% decrease in the initial current after 5 days was noticed. The operational stability of the electrode was further examined by using the same electrode for long time and it was found that there is no observable change in the initial amperometric current (Supporting information).

3.4. Biosensing of glucose

The analytical application of the nanoparticle-based platform in the development of oxidase-based biosensor was examined by taking GOD as a model system. H_2O_2 is generated during the reaction of oxidase enzymes with substrate in the presence of oxygen. The concentration of substrate in the sample can be quantified by measuring the enzymatically generated H_2O_2. The electrode which has high sensitivity towards enzymatically generated H_2O_2

Table 1
Electrochemical sensing of H_2O_2 using different Pt nanoparticle-based electrodes.

Electrode	Detection potential (V) (Ag/AgCl)	Linear range	LOD (nM)	Reference
Polymer/Pt nanoparticle[a]	0.6	42 nM to 0.16 mM	42	Karam and Halaoui (2008)
Pt nanowire[b]	0	0.1–60 mM	50	Yang et al. (2006)
CNT/nano-Pt[a]	0.55	25 nM to 2 mM	25	Male et al. (2007) and Hrapovic et al. (2004)
Carbon film/nano-Pt[a]	0.6	0.5 μM to 2 mM	7.5	You et al. (2003)
Ensembles of nano-Pt[a]	0.5	0.5 nM to 4 mM	0.5	Present work

[a] Sensing of H_2O_2 by its oxidation.
[b] By its reduction.

can be used in the fabrication of sensor devices. In the present investigation, as the nanoparticle-modified electrode is highly sensitive and stable towards H_2O_2, it has been used as a sensitive transducer in the development of glucose biosensors. GOD was immobilized on the nanoparticle-modified electrode by casting 10 μL (4 U/μL in 5 mM PBS) and dried at 4 °C for 45 min. The potential of the GOD immobilized electrode was held at 0.5 V and aliquots of glucose was injected into oxygen saturated PBS at regular intervals (Supporting information). This electrode could successfully detect enzymatically generated H_2O_2. The sensitivity of the electrode towards glucose was obtained from the calibration plot and was 0.0187 μA/μM (R^2 = 0.99). The electrode is highly sensitive and it shows linear response towards glucose. The limit of detection was 90 nM (S/N = 3). The apparent Michaelis-Menten constant (K_M^{app}) for the enzymatic reaction was calculated from the double reciprocal plot and was 212 μM, which is in close agreement with the previous reports (Crespillo et al., 2008; Alonso et al., 2004).

4. Conclusion

Pre-organized metal precursors were chemically reduced to generate ensembles of metal nanoparticle on the electrode surface. The nanoparticle-based platform has been used in the development of highly sensitive sensor for H_2O_2 without any redox mediator or enzyme. The sensor is highly sensitive, stable and it could detect as low as 0.5 nM (S/N = 5) of H_2O_2. The analytical utility of the electrode in the development of amperometric biosensors was examined by taking glucose oxidase as a model system. The pre-organization of the metal precursor on the transducer paves the way for the generation of ensembles of nanoparticle. As the nanoparticle-modified electrode is highly sensitive and show linear response, it may find application in the development of sensors and biosensors for biologically important analytes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2009.04.015.

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