



Polyvinylpyrrolidone stabilized palladium nanospheres as simple and novel electrochemical sensor for amperometric hydrogen peroxide detection



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ABSTRACT

A simple and cost-effective method for the synthesis and stabilization of palladium nanospheres is proposed to fabricate an effective sensor for electroanalytical determination of hydrogen peroxide (H_2O_2). UV-visible spectroscopy and X-ray diffraction confirm the presence of palladium nanoparticles (Pd NPs), and Fourier transform infrared (FTIR) spectrometry validates the protective action of polyvinylpyrrolidone (PVP) towards the NPs. The size and morphology of the Pd NPs were investigated using transmission electron microscopy (TEM). The electrochemical characteristics of the electrode that is modified using PVP stabilized palladium nanospheres are evaluated using cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS). The optimized sensor exhibits unique sensing performance towards hydrogen peroxide detection. The versatility of the sensor is demonstrated by the detection limit down to 8 nM with a quick response time of 3 s and a good linear range of 0.01–1 μM . In addition, the sensor also displayed good selectivity against interfering electroactive species such as ascorbic acid (AA), uric acid (UA) and acetaminophen (AP). The simplicity in the synthesis methodology and substrate fabrication along with attractive features such as lower limit of detection (LOD), wide linear range, good reproducibility and long-term stability make the proposed sensor a promising candidate for potential applications in H_2O_2 analysis.

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1. Introduction

Hydrogen peroxide (H_2O_2) detection has become an area of increased importance as the excess production of H_2O_2 leads to the development of numerous diseases such as diabetes, aging and atherosclerosis [1]. H_2O_2 is associated with physiological and pathological conditions of the living system [2]. In addition, H_2O_2 plays significant roles in chemical, biological, food, clinical and environmental control applications [3–5]. Electrochemical amperometry technique is found to be an excellent tool for the determination of H_2O_2 [6], as other methods such as chemiluminescence [7], titrimetry [8], photometry [9] and high performance liquid chromatography [10] are not capable of detecting trace concentrations of H_2O_2 and suffer from the interference of other biologically active molecules [11]. Electrodes modified with noble metal nanoparticles have attracted greater attention [12] for their favorable performance as sensors, owing to their ultra-high sensitivity, extraordinary electrocatalytic activity and large specific surface area [12], as the presence of tiny conduction centers in them

facilitates electron transfer processes [13–15]. In spite of the significant roles played by metal nanoparticles in various fields, the major drawback in employing nanomaterials is that they have an innate tendency to agglomerate [16]. This can adversely affect the performance of the sensor, resulting in poor electrocatalytic activities. Prevention of aggregation, undesired growth, and precise control of particle size will help retain the unique nature of the nanoparticles. This is made possible by employing polymers [17], dendrimers [18], surfactants [19], gels [20] and ligands [21] in which these nanoparticles can be stabilized. However, these stabilizers get adsorbed on the surface of nanoparticles, hampering their catalytic activities [22]. But vinyl polymers possess the ability to retain the inherent catalytic activity of the metal nanoparticles intact [23] and the protective characteristics of these polymers outshine other stabilizers [24]. The chemical stability and the affinity of PVP vinyl polymer towards metals make it a widely preferred one in the process of stable dispersion of metal nanoparticles [25]. The functional groups in PVP such as C=O, N and long polymer chains aid in the stabilization of metal nanoparticles [26]. In addition, PVP is a promising material in biosensor applications as it has a good water solubility, biodegradability and biocompatibility [27].

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Palladium NPs have gained greater attraction of researchers in recent years for their role in catalytic applications for many organic reactions [28], purification catalysis [29], surface enhanced Raman scattering [30], electrochemical detection [31] and as electrocatalyst for oxygen reduction [32–34]. Palladium nanoparticles are preferred over other noble metal nanoparticles for electrode modification since they exhibit superior electrocatalytic activity towards H_2O_2 reduction [35,36] and show both enhanced electron transfer and reduced overpotential [37]. Moreover, the abundance of Pd over other noble metals makes it a cheaper substitute for utilization in various fields [38]. But there are only few reports, involving Pd for H_2O_2 reduction. The papers reported recently involved carbon nanotubes (CNTs) [39–41], graphene [38,42,43], TiO_2 [44] and conducting polymers [45] to enhance the electrocatalytic activity of Pd NPs. In most cases, the preparation procedure is costly and involves complex and complicated processes for the synthesis of nanoparticles. In addition, most of the routes followed are time-consuming and tedious. In the following paragraph, we discuss the methods and procedures used in the recent scholarly reports for the synthesis of nanoparticles to be used in H_2O_2 sensing.

You et al. [41] have made use of multi-walled carbon nanotubes (MWCNTs) with Pd NPs for the electrocatalytic reduction of H_2O_2 . Chen et al. [38] used homogeneous GNs suspension and K_2PdCl_6 to prepare PdNPGNs nanocomposite for electrochemical sensing of H_2O_2 . Rajkumar et al. [39] have used facile electrochemical method to prepare Pd nanourchins decorated MWCNTs for electrocatalytic reduction of H_2O_2 . Sun et al. [42] prepared hydrogen peroxide biosensor, based on direct electrochemistry of hemoglobin in Pd NPs/graphene–chitosan nanocomposite film. Nandini et al. [43] utilized Pd NPs, graphene and an enzyme, horseradish peroxidase (HRP) for selective determination of H_2O_2 by codeposition of Pd and HRP on functionalized graphene-modified electrode. Kong et al. [44] prepared TiO_2 /Pd composite hollow spheres using solvothermal treatment to fabricate non-enzymatic H_2O_2 biosensor. As observed, most of the work reported in the literature used carbon based nanomaterials such as CNT, graphene and/or enzymes along with Pd NPs to enhance the electrochemical sensing of H_2O_2 . Though works reported by Kong [44] and Jiang et al. [45] involved simple one-pot method, the synthesis process took more than 3 h and involved costly chemicals such as TiO_2 and conducting polymers besides Pd NPs. In our work, we have attempted a simple, rapid and cost-effective method to prepare Pd NPs stabilized in PVP matrix and we could obtain a better detection limit and good sensitivity.

This paper presents a simple two step methodology adopted for the synthesis of Pd NPs. Sodium borohydride is used as a reducer and PVP as the stabilizing agent. PVP is one of the polymers extensively used for Pd NPs stabilization [46–50]. This Pd NPs-modified electrode exhibits a lower detection limit, wide range of linearity, good stability and selectivity. To the best of our knowledge, this work is an improvement over the Pd NPs based electrochemical sensors. Here we could obtain very low detection limit even without the aid of enzymes or CNTs or conducting polymers. The methods and results are discussed in the following sections.

2. Experimental procedures

2.1. Materials and methods

Palladium chloride (PdCl_2), sodium dihydrogen phosphate (NaH_2PO_4), and disodium hydrogen phosphate (Na_2HPO_4), were purchased from Merck (Mumbai, India). Sodium borohydride (NaBH_4), polyvinylpyrrolidone (PVP K 40) and nafion were obtained from Sigma Aldrich (USA). Hydrogen peroxide (30% w/v) was purchased from SD Fine Chemicals (Mumbai, India). All glasswares were washed with aqua regia and dried in an oven prior

to use. The chemicals used were of analytical grade and deionized water was used throughout the experiment.

2.2. Synthesis of Pd NPs

Palladium chloride was reduced by NaBH_4 into palladium nanospheres and was stabilized by vinyl polymer polyvinylpyrrolidone. In a typical synthesis, palladium nanospheres were prepared by dissolving PdCl_2 (1 mM) in 25 mL of 0.2 M HCl until the metal salt is completely dissolved. As a result, a bright orange solution was obtained. NaBH_4 was ice-cooled for 1 h before using it as a reductant for Pd NPs synthesis. Then 500 μL of ice-cooled NaBH_4 solution was added to the bright orange PdCl_2 solution and the solution instantly turned into dark brown, which is typical of Pd NPs [47]. Within seconds of synthesis of Pd NPs, 5 mL of PVP solution was added to the nanocolloid. Here, PVP acts as a stabilizer that would prevent the nanoparticles from agglomeration. Even a slight delay would result in the aggregation and growth of NPs. When the metal NPs are not protected by vinyl polymer PVP, the characteristic dark brown solution of the Pd NPs changes into grayish black as shown in the schematic diagram of Fig. 1. This indicates the solution was unstable in the absence of PVP and hence resulted in precipitation of palladium particles. These results clearly imply that the electrostatic stabilization provided by NaBH_4 is guaranteed only for a short period of time, while PVP polymer provides long time steric stabilization and prevents the nanoparticles from growth and aggregation. The process is shown in Fig. 1 as a schematic diagram.

2.3. Instrumentation and measurements

The presence of palladium nanoparticles was confirmed by UV–visible absorption studies employing JASCO V-630 spectrophotometer. The presence and phase purity of the nanoparticles are analyzed by X-ray diffraction patterns with an XPERT-PRO diffractometer using a Cu $\text{K}\alpha$ source operated at 40 kV and 30 mA with $\lambda = 1.540 \text{ \AA}$. The protective action of the stabilizing agent towards the NPs was determined by FTIR spectroscopy using Perkin-Elmer Spectrum BX II spectrometer. The size and morphology of the prepared nanoparticles were analyzed using transmission electron microscopy (TEM) with a JEM 3010, JEOL Transmission Electron microscope operated at 200 kV.

Electrochemical studies such as cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy were performed on a CHI workstation (CHI 600D), with a three electrode system comprised of platinum wire as counter electrode, Ag/AgCl as reference electrode and Pd nanospheres-modified glassy carbon electrode (GCE, 3 mm diameter) as the working electrode. Glassy carbon electrodes were polished successively using 1, 0.3, 0.05 μM alumina slurry and then thoroughly rinsed with deionized water. All the electrochemical measurements were carried out in 0.02 M PBS (pH 7). Prior to measurements, the solution was deoxygenated with nitrogen gas.

The sensor for the determination of H_2O_2 was prepared by dropping 10 μL of PVP stabilized Pd nanocolloidal solution onto the GCE electrode with the aid of a micropipette and was allowed to dry at room temperature for 1 h. Then 5 μL of 0.05% nafion solution was dropped onto the above electrode as a fixative to form a strong and durable film. The loading of Pd NPs on GCE is estimated to be $4.9 \times 10^{-3} \text{ mg cm}^{-2}$.

3. Results and discussion

3.1. Optical and structural studies

The presence of palladium nanoparticles in the nanocolloid was supported by UV–visible absorption studies (Fig. 2). UV–visible

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