Sensors and Actuators B 193 (2014) 149–156

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Preparation of vinyl polymer stabilized silver nanospheres for electro-analytical determination of H_2O_2

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ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form 30 October 2013
Accepted 24 November 2013
Available online 1 December 2013

Keywords:
Silver nanoparticles
Polyvinyl pyrrolidone
Hydrogen peroxide sensor
Electrochemical studies

ABSTRACT

Silver nanoparticles (NPs) embedded in polyvinyl pyrrolidone (PVP) were synthesized using a simple route for the fabrication of hydrogen peroxide (H_2O_2) sensor. UV–vis spectroscopy and X-ray diffraction analysis confirmed the presence and crystalline nature of the silver nanoparticles. The morphology of the material was investigated by transmission electron microscopy (TEM). The electrochemical properties were characterized by cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS). The fabricated sensor showed a significant catalytic activity towards H_2O_2 reduction, attributable to silver nanospheres protected by vinyl polymer. The sensor responds to H_2O_2 in a wide linear range and the detection limit was 40 nM which is lower than most of the silver NPs based sensors reported recently. The sensor exhibits good selectivity, reproducibility and long term stability with a swift response time of 2 s.

1. Introduction

Detection of hydrogen peroxide (H_2O_2) has attracted a great deal of attention now-a-days owing to its widespread use in applications in the field of biology, medicine, food and industry [1–4]. Due to its environmentally sound behaviour and its effectivity as an antimicrobial agent, which kills germs by oxidation process [5–7], H_2O_2 is used as a sterilant in packaging and handling of foods [8], drugs and medical equipments [9,10]. Besides, the most valuable property of H_2O_2 is that it decomposes into harmless products of water and oxygen [11] unlike other sterilants which result in toxic compounds [10]. Additionally, as a by-product of oxygen metabolism, it is also naturally produced in living organisms [12]. Because of its varied uses in physiological as well as non-physiological fields, it becomes necessary to accurately determine this important analyte, H_2O_2, in trace concentrations. Many detection methods and schemes such as fluorimetry [13], spectrophotometry [14], chemiluminescence [15] and titrimetry [16] are employed for the detection of H_2O_2. But among these techniques, electrochemical technique is the most preferred one because of its simplicity in mode of operation, cost effectiveness, low detection limit, good sensitivity and selectivity [17–20].

In general, nanomaterials play a vital role in electroanalysis in improving the novelty of the sensor [21,22]. Especially noble metal nanoparticles such as gold [23], platinum [24], silver [25] and palladium [26] plays a significant role in improving the performance of the H_2O_2 sensors because of their large surface area to volume ratio, convenience of electron transfer, excellent conductivity and electrocatalytic activities [7,19,27,28]. Among the noble metals, silver nanoparticles display excellent electrocatalytic ability towards the reduction of H_2O_2 [29–31]. Good conductivity and availability of larger paths for charge transport channels make silver nanoparticles as attractive tools to enhance the electron transfer reaction between H_2O_2 and silver NPs [32]. In addition, Ag NPs are found to be highly sensitive, biocompatible and cost effective when compared to other noble metal nanoparticles [33].

The extremely small size, high surface energy and large number of dangling bonds [34,35] make the nanoparticles susceptible to aggregation. Hence the physical and chemical properties of the naked NPs differ and especially their effectiveness as catalyst will also suffer considerably [36]. Therefore it is of utmost importance to protect the colloid from aggregation. The aggregation of metal nanoparticles can be prevented either by electrostatic stabilization or by steric stabilization [37]. Combination of these two stabilization mechanism is also possible, known as electrosteric stabilization, which is employed in the present work.

There are number of reported works on noble metal based nanostructured materials towards electroanalytical determination of H_2O_2. Several researchers have used core and yolk shell nanostructures to enhance the electrocatalytic activity of the noble metal based sensors. Li et al. [38] used platinum-coated gold nanoparticles with core@shell structure while Zhou et al.

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http://dx.doi.org/10.1016/j.snb.2013.11.083

[39] employed Au-Cu_xOS yolk shell nanostructure for ultrasensitive H_2O_2 detection. There are also numerous reports on the improved performance of the sensor with immobilization of enzymes (haemoglobin, horseradish peroxidase) at the surface of the noble metal NPs [40–42]. Though enzymes improve the performance of the sensor, they suffer from denaturation and hence the long term stability of the sensor is affected to a larger extent. Several of the workers have relied heavily on carbon nanostructures such as graphene, carbon nanotubes along with noble metals [43–46] towards the fabrication of sensors. Liu et al. [43] have attempted to fabricate a sensor based on an enzyme-free tricomponent nanohybrid. Rajkumar et al. [44] have electrochemically synthesized palladium decorated multiwalled carbon nanotubes while You et al. [45] have reduced graphene oxide that has been functionalized with aminothiophenol-Pd NPs as a hydrogen peroxide sensor. The chemicals employed by these workers are costly. Further, the experimental technique adopted are time consuming and tedious. Guascito et al. [47] have used soft solution technique to prepare silver nanoparticles capped in polyvinyl alcohol. The synthesis methodology adopted by them is extensive and involved heating procedure. The time required for the synthesis also took longer hours. The present work provides a simple, low-cost and quick synthesis procedure compared to most of the works reported in the literature. The detection limit obtained in the present work is also one of the lowest obtained in the recent past.

Recently Zhao et al. [28] and Wang et al. [48] employed PVP (polyvinyl pyrrolidone) as protecting agent for Ag NPs to be used in H_2O_2 sensing. Wang et al. have indulged in a complex synthesis methodology which involved water-cooling, followed by heating in an oil bath and subsequent Argon stream treatment. This process is cumbersome and is time consuming, in addition to being a costly route to prepare silver NPs. In the present work we have adopted a simple, two step quick process that took less than 30 min for synthesis. The nanocubes obtained by Wang et al. are around 45 nm while flower like morphology obtained by Zhao et al. is around 1.5 μm. We could obtain nanospheres of about 10 nm diameter with good dispersion in PVP. These nanoparticles have been found to exhibit lower detection limit (LOD = 40 nM) with an excellent sensing ability than those attained with nanocubes (LOD = 180 nM) by Wang et al. and flowerlike microspheres (LOD = 1.2 μM) by Zhao et al. Here it is clear that the size of the particle have played a unique role in achieving lowest detection limit for H_2O_2 sensing.

In this paper, we present a detailed account on the synthesis and stabilzation of silver NPs and the electrochemical studies were made on the PVP stabilized silver nanoparticles (PSSN) to assess their suitability towards the detection of H_2O_2. From the electrochemical studies, the proposed sensor is found to be sensitive, stable, efficient, reliable and showed very good catalytic ability towards H_2O_2 reduction.

2. Materials and methods

2.1. Chemicals

Analytical grade silver nitrate ($AgNO_3$, 99%), sodium borohydride ($NaBH_4$, 98%), polyvinyl pyrrolidone (PVP K 40), and nafion were obtained from Sigma–Aldrich and were used as received. H_2O_2 (30% w/v), sodium hydrogen phosphate (NaH_2PO_4, 99%), disodium hydrogen phosphate (Na_2HPO_4, 99.5%) and *n*-propanol were purchased from Merck. Deionized water was used throughout the experiment. All the glass wares were washed with non-ionic detergent and aqua regia followed by thorough rinsing with deionized water and dried in an oven prior to use.

2.2. Synthesis of vinyl polymer stabilized metal NPs

In a typical synthesis, silver nitrate ($AgNO_3$) reduction was carried out using sodium borohydride ($NaBH_4$). Excess of $NaBH_4$ is needed to both reduce and stabilize the silver NPs. Thus the molar ratio of $NaBH_4$ taken was five times that of $AgNO_3$. The chemical reaction between $AgNO_3$ and $NaBH_4$ can be explained as [49].

$$AgNO_3 + NaBH_4 \rightarrow Ag + 1/2H_2 + 1/2B_2H_6 + NaNO_3 \quad (1)$$

A second solution was prepared by dissolving 20 mg of PVP (0.2 mM) in 25 mL of *n*-proponal and water taken in equal ratio and was stirred gently for 1 h. To prevent aggregation, the preformed NPs solution was quickly added into the PVP solution and was stirred vigorously for 30 min. The resulting colloid exhibited a pale yellow colour appearance. The detailed step by step procedure is shown in Fig. 1 as schematic diagram.

After the completion of the reaction, the collodial solution was stored in an amber glass container to prevent any interaction of silver NPs with the light from the surrounding environment.

2.3. Preparation of vinyl polymer stabilized silver NPs sensor

Prior to modification of electrode, GCE was polished successively with 1.0, 0.3, 0.05 μm alumina powder and further washed in absolute ethanol and deionized water.

Then 10 μL of solution containing PSSN was directly dropped onto the polished GC electrode and was allowed to dry at room temperature for 1 h. 5 μL of 0.05% nafion was pippetted onto the electrode surface to form a strong and a durable film of PSSN on the electrode.

Nafion polymers are a family of perfluorinated anionic polyelectrolytes. The nafion polymer is reported to have high chemical stability, excellent biocompatibility, and anti-interference property against many of the biological macromolecules [50,51]. In addition to that, it also improves the long term stability of the sensor [52].

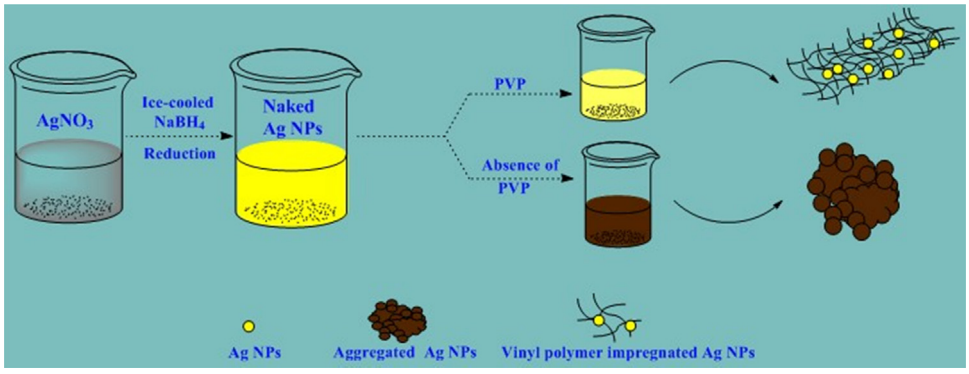

Fig. 1. Schematic diagram on the formation of silver nanoparticles protected/unprotected by vinyl polymer.