



Metal-ion co-ordination assembly based multilayer of one dimensional gold nanostructures and catalase as electrochemical sensor for the analysis of hydrogen peroxide



Seetharamaiah Nandini^{a,b}, Seetharamaiah Nalini^{a,b}, Pathappa Niranjana^{b,*},
Jose Savio Melo^{c,*}, Gurukar Shivappa Suresh^{a,*}

^a Department of Chemistry and Research Centre, N.M.K.R.V. College for Women, Jayanagar, Bangalore, 560 011, India

^b Department of Biochemistry, Kuvempu University, Shankarghatta, Shimoga, 577451, India

^c Nuclear Agriculture and Biotechnology Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India

ARTICLE INFO

Article history:

Received 24 June 2016

Received in revised form 30 January 2017

Accepted 1 February 2017

Available online 2 February 2017

Keywords:

Metal-ion co-ordination

Multilayer assembly

Catalase

1D gold nanostructures

Cobalt nanoparticles

Electrochemical biosensor

ABSTRACT

In this study, we present for the first time an electrochemical biosensor for the quantification of hydrogen peroxide (H_2O_2) based on one dimensional gold nanostructures (1D-AuNs) and catalase (CAT) multilayer-by layer film fabricated on graphite electrode (GE) through metal-ion co-ordination assembly technique. Synthesis of 1D AuNs was performed by template directed synthesis employing cobalt nanoparticles as sacrificial templates. Characterization of the AuNs using UV-vis spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) clearly demonstrated the successful formation of nanostructures. Besides, the multilayer-by layer film was evaluated in terms of number of layers and electrochemical behavior using electrochemical quartz crystal microbalance (EQCM), UV-vis spectroscopy, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). In addition, the fabricated multilayer film was evaluated for electrocatalytic analysis of H_2O_2 using CV, differential pulse voltammetry (DPV) and chronoamperometry. CV assay indicates that a direct electron transfer is accomplished between the CAT and the electrode surface through metal-ion co-ordination assembly technique. Also, we determined the optimal operating potential and electrolyte pH to avoid possible interfering substances. The proposed biosensor showed superiority over previously reported electrochemical biosensors in the analytical characteristics such as rapid response (5 s), wide linear range (0.05–19.35 mM), high sensitivity ($992 \mu A^{-1} mM^{-1} cm^{-2}$) and low detection limit (0.98 nM). The apparent Michaelis–Menten constant (K_m^{app}) which gives an evidence of enzyme affinity of the biosensor was estimated to be 0.21 mM indicating high affinity for H_2O_2 . The excellent anti-interference ability of the biosensor is also presented. Moreover, the proposed biosensor illustrated good repeatability, reproducibility, admirable electrochemical and long-term stability.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The quantitative analysis of hydrogen peroxide (H_2O_2) has become extensively studied subject of interest in the field of clinical diagnostics, chemical, biological, food and pharmaceutical industries [1,2]. H_2O_2 is a multifunctional oxidizing agent that has aroused a great deal of practical attention for the past decade since it is not only an important intermediate of several enzymes catalyzed biological reactions, but is employed in waste

water treatment, in textile industries and also in organic synthesis [3,4]. In contrast, this well-known reactive oxygen species are also considered hazardous as it can cause brain damage, affects the central nervous system, etc. As a consequence, the development of reliable, simple, rapid and precise analytical methods for the monitoring of H_2O_2 becomes significant and of concern. A number of analytical techniques such as titrimetry, spectrophotometry, chemiluminescence and electrochemistry [5,6] have been applied for this purpose. Amongst these, the application of electrochemical methods, in particular enzymatic electrochemical detection of target molecules is the most promising assay due to its high specificity, sensitivity, accuracy, rapidness, requirement for low volume of analyte and simplicity [7,8]. Hitherto, survey of the literature reveals the application of heme containing proteins (hemoglobin,

* Corresponding authors.

E-mail addresses: bpniru@gmail.com (N. Pathappa), jsmelo@barc.gov.in (S.M. Jose), sureshsmrv@yahoo.co.in (S.S. Gurukar).

myoglobin) and enzymes [horseradish peroxidase (HRP), catalase (CAT)] as the bioelectrocatalyst in the H_2O_2 determination [9–12]. Perpetually, CAT (EC 1.11.1.6) has prompted to be an important oxidoreductase enzyme to contain the highest turnover numbers of all enzymes, i.e., one molecule of this heme containing redox protein can catalyze five million molecules of H_2O_2 to oxygen and water per second without the formation of free radicals. CAT is present in all aerobic organisms. It comprises of ferriprotoporphyrin IX at its redox centre and a heme prosthetic group at its active site with metallic iron (Fe_{II}) with a molecular weight of ~ 240 kDa. Unfortunately, biocatalyst immobilized on transducers often encounter hindrance in the electron flow between the electrode and the surface owing to the deep entombment of the electroactive prosthetic groups inside the polypeptide chain, adsorptive denaturation and unfavorable orientation of the enzymes [13]. To prevail over these problems, it is imperative to formulate novel and facile immobilization matrices that can surpass these limitations. Among a variety of immobilizing materials, nanostructured materials have been acknowledged as “electron conducting wires” and typical immobilization platforms to achieve direct electron transfer reactions, amplify the analytic signal of the biorecognition events and offer favorable microenvironment for the bioelement. In recent years, there have been remarkable efforts and interest endowed in the development of metal nanostructures owing to their dominating size and shape dependant physiochemical properties. Many research articles accentuating the tremendous application of these metal nanostructures in electronics, catalysis, energy, material chemistry, sensing biology have been reported [14–16]. Among these emphases has been established in the field of electrochemistry for the fabrication of biosensors due to their biocompatibility, non toxicity, high affinity, etc. Further, compared with zero dimensional, two dimensional and three dimensional nanostructures, many researchers have set one dimensional (1D) metal nanostructures as their main focus of investigation as these materials offer an important prospectus to interconnect the functional units in electrochemical and electromechanical devices [17]. Therefore, cost effective synthetic procedures are being desired by material scientists. Studies have shown and established synthetic procedures for a broad class of 1D metal nanostructure such as chemical vapor deposition, lithography, surfactant assisted chemical synthesis etc. [18–20]. Despite this, the template directed synthesis is an efficient, simplified and convenient procedure in which the template or the host material directs and controls the growth of the desired material yielding well ordered nanostructures following template elimination [21]. Martin documented the first report demonstrating the synthesis of nanostructures using as track-etched polycarbonate membrane or porous alumina membrane [22]. Since then, extensive synthetic template directed approaches have been adopted. There are a large number of hard (polymeric membrane, zeolite, existing nanostructures synthesized from other approaches, carbon microspheres [23–25]) and soft materials (copolymer complex micelles, polyelectrolyte aggregates, CTAB [26,27]) that might be used as templates. Similarly, in our previous research work, one dimensional Au nanostructures were successfully synthesized exploiting peptide nanotubes as an effective template [28,29]. One particular experimental demonstration by Liang et al. for Co NPs as a classical example of a unique class of template for the fabrication of perfect hollow metal nanotubes such as gold, palladium and platinum has attracted researchers from diverse areas [30–32]. Typically, the advantages of exploiting CoNPs as sacrificial template is its high chemical reactivity, non toxicity, yielding of high quality crystalline metal nanotubes with no need for chemical derivatization of the template. CoNPs are apparently considered as the best template for the fabrication of 1D gold (Au) nanostructures by means of galvanic displacement because Co is oxidised at the same time at which Au(III)

is reduced, resulting in hollow tubular nanomaterials owing to the reduction potential of $\text{AuCl}_4^-/\text{Au}$ (0.99 V vs. SHE) that is more positive than that of Co_2^+/Co (-0.28 V vs. SHE) [33]. The use of Au nanostructures in electrochemical biosensors has proven to be highly versatile and favorable since they show high catalytic activity, inertness, biocompatibility, etc. Moreover, the amine and cysteine groups of the enzyme can attach strongly to Au nanostructures via covalent forces rendering enzyme immobilization stable. However, there are challenges for integrating the metal nanostructures with enzymes onto an appropriate support. So, novel attachment strategies are desired to append nanomaterials and enzymes with the transducer in proper orientation for continuous usage. The diverse strategies employed for the construction of electrochemical biosensor are self assembly method, layer-by-layer technique, Langmuir-Blodgett approach, spin coating and casting [34]. It has been recognized that layer-by-layer assembly technique (LBL) is powerful and widely applicable procedure for constructing well-ordered functional multilayer films on the electrode surface with precise control over the layer composition, number and thickness. LBL technique which enables the formation of multilayer structures in a reproducible way can be produced by means of electrostatic interactions, covalent bonding, hydrogen bonding and metal co-ordination interactions. In particular, metal co-ordination self assembly based on sequential and alternative binding of metal ions and organic ligands is a convenient approach for the construction of multilayer films. In the past decade, pioneering work on co-ordination assembly using hydroxamate and metal ions was demonstrated by a group of researchers led by Prof. I. Rubinstein. They showed ligand-metal specificity, effective tuning of the compositional, structural, mechanical, electrical, and optical properties of the resulting potentially useful nanostructures [35–37]. There are compelling evidence provided for the application of LBL technique in the preparation of multilayer films using electrostatic force for the detection of glucose [38], lactic acid [39], H_2O_2 [40], or using covalent binding for the detection of *p*-Aminophenol [41], etc. Similarly, our group had reported the successful electrochemical detection of acetaminophen [42], simultaneous detection of ascorbic acid, uric acid and dopamine [43] and direct electrochemistry of cholesterol oxidase [44] using multilayer films developed by LBL technique. Although remarkable advancements have been made in the LBL technique for the fabrication of electrochemical biosensors with novel properties like control of molecular architecture and its properties, such as charge, thickness, polarity and roughness of the multilayer films [45], no adequate reports on metal-ion co-ordination assembly for the development of electrochemical biosensor is exploited so far.

In this context, as an extension of our previous work, the present article is aimed at investigating the metal-ion coordination assembly strategy in electrochemical applications using Au nanostructures. To achieve this goal, 1D gold nanostructures were synthesized using CoNPs as sacrificial template via galvanic displacement method under optimized conditions. The formation of Au nanostructures obtained from the so-called “core-shell” configuration was monitored using UV–vis spectroscopy. The structural, chemical and morphological evaluation of the Au nanostructures was systematically probed using XRD, SEM and EDAX. An attempt was then made to fabricate an electrochemical biosensor using sequential alternative assembly of dimethylhydroxamate (Ligand 1), Ti(IV)isopropoxide, tetrahydroxamate (Ligand 2), 1D Au nanostructures and CAT on the surface of Poly(Tyr) which was previously deposited on graphite electrode (GE). In this regard, the Ligand 1 and Ligand 2 were used as anchor and spacer molecules respectively. To the best of our knowledge this is the first report on the application of metal-ion coordination assembly for electrochemical biosensor in the detection of H_2O_2 . This novel tri-layered film was characterized using UV–vis spectroscopy, EIS and EQCM.

Download English Version:

<https://daneshyari.com/en/article/5009940>

Download Persian Version:

<https://daneshyari.com/article/5009940>

[Daneshyari.com](https://daneshyari.com)