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A novel multivalent nanomaterial based hydrogen peroxide sensor

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Abstract

Most of the H_2O_2 biosensors developed till date are based on enzymes and proteins causing them to have a limited lifetime. Moreover, complex procedures are followed for sensor fabrication. Therefore an inorganic material based sensor, with a simple design and longer shelf-life is highly desirable. In this work, an electrochemical microsensor has been designed, fabricated and tested for hydrogen peroxide detection. The 3–5 nm, non-agglomerated cerium oxide particles were synthesized and integrated with the microsensor. This greatly increases the sensor lifetime, sensitivity and robustness. The sensor is characterized and tested using samples from 1 μM to 30 mM H_2O_2 range and a linear response is observed. Miniaturization, low detection limits, high sensitivity as well as ease of fabrication are some of the advantages of this work. Same principle could be extended for the detection of other free radicals as well.

Keywords: Electrochemical microsensor; Nanoceria; Free radical; Amperometric; Hydrogen peroxide

1. Introduction

Ever since aerobic respiration caused an increase in partial pressure of oxygen in the atmosphere around 2.5 billion years ago [1], organisms have adapted to detoxify the reactive oxygen species produced as by-products of metabolism or as product of environmental stress. They perform this function by sensing the presence of reactive oxygen species and activating specific signal transduction pathways in response. Many organisms have also harnessed reactive oxygen species for use as signaling and defense molecules. Both plants and animals produce reactive oxygen species as a response to pathogen attack. Hydrogen peroxide is one of the abundant forms of reactive oxygen.

It plays a significant role in cell biology for defense mechanism against pathogens [2]. H_2O_2 released by various environmental and developmental stimuli can act as a signaling molecule that regulates cell development, stress adaptation and programmed cell death [3]. H_2O_2 is also produced in many aerobic processes and as intermediates in enzymatic reactions. Transfer of a single electron often catalyzed by metals such as Fe and Cu, to O_2 forms the super-oxide radical, $O_2^{\bullet -}$. $O_2^{\bullet -}$ disproportionate in aqueous solutions, to form hydrogen peroxide. Further disassociation of H_2O_2 can form extremely reactive hydroxyl free radicals ($OH^{\bullet}$) [4].

Hence, the detection of H_2O_2 has direct ramifications for hydroxyl free radical detection, and the same approach can be applied to the detection other free radicals as well. For H_2O_2 measurement, enzyme-modified electrodes are frequently used, which utilizes direct electron transfer between the enzyme and electrodes [5,6]. However, the immobilization and stabilization protocol of the enzyme is very complicated. In this type of sensor, long-term stability, reproducibility and renewability of the sensor surface are great concerns. In our microsensor, unique multivalent and regenerative properties of nanoceria particles are utilized to record the electron transfer from H_2O_2 directly without resorting to the complex enzyme preparation steps [7]. In addition, sensor surface is renewable, leading to long-term stability.

2. Nanoparticle synthesis

Non-agglomerated cerium oxide nanoparticles with a uniform particle size of 3–5 nm were synthesized using water-in-oil

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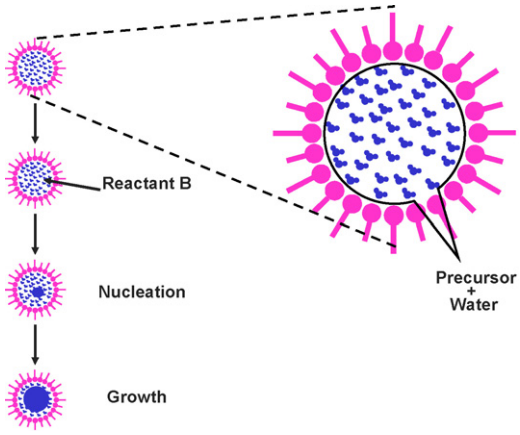

Fig. 1. Nanoparticles synthesis using reverse micelle process.

microemulsion technique as shown in Fig. 1. The nanosized micelles act as nanoreactors for nanoparticle formation. The microemulsion system consisted of the surfactant, sodium bis(2-ethylhexyl) sulphosuccinate (AOT), toluene and water. All the chemicals were purchased from Aldrich Chemicals Company Inc. Details of the synthesis are published elsewhere [8]. Nanosized reverse micelles control the particle size and agglomeration. The nanocrystalline ceria sensor senses the free radicals through surface chemical and complexation reactions.

3. Nanoparticle characterization

The particle morphology was studied using high-resolution transmission electron microscopy (HRTEM). The surface chemistry of the ceria particles was studied using X-ray photoelectron spectroscopy (XPS). The ceria nanoparticles were deposited on the carbon coated copper grid for HRTEM analysis by the dip coating method. The HRTEM images of the as prepared particles were obtained with a Philips (Tecnai Series) transmission electron microscope operating at 300 keV. The XPS data was obtained using a 5400 PHI ESCA (XPS) spectrometer. The base pressure during XPS analysis was 10^{-9} Torr and Mg Kα X-ray radiation (1253.6 eV) at a power of 200 W was used. The binding energy of the Au ($4f_{7/2}$) at 84.0 ± 0.1 eV was used to calibrate the binding energy scale of the spectrometer. Any charging shift produced in the spectrum by the sample was carefully removed by taking C 1s position (284.6 eV) as a reference line as shown by Barr and Seal [9]. XPS spectra smoothening and baseline subtraction was carried out using PeakFit (Version 4) software. X-ray photoelectron spectroscopy (XPS) analysis was conducted to confirm the presence of multivalent cerium ions [10].

4. Synthesis results

Cerium oxide nanoparticles prepared by the microemulsion process results in ultra fine, non-agglomerated particles in the range of 3–5 nm [5,8]. The synthesized nanoparticles were characterized for morphology and surface chemistry by high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). The HRTEM image as shown in Fig. 2 indicates the formation of uniformly distributed, non-agglomerated nanoparticles of Cerium oxide in the range of 3–5 nm. The XPS spectrum shown in Fig. 3 corroborates the presence of a mixed valence state (Ce^{3+} and Ce^{4+}) for the synthesized cerium oxide nanoparticles. This result is similar to previously published results [9].

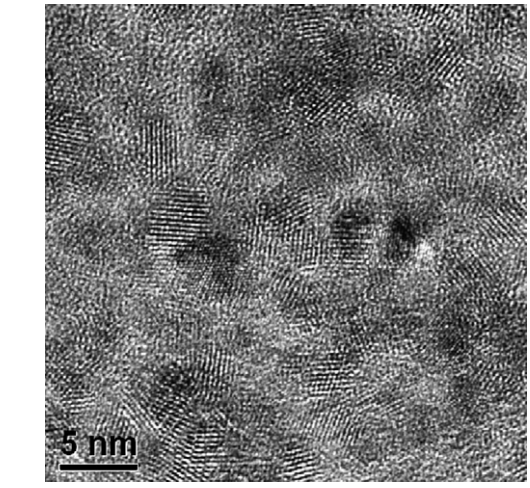

Fig. 2. HRTEM image of nanoceria particles.

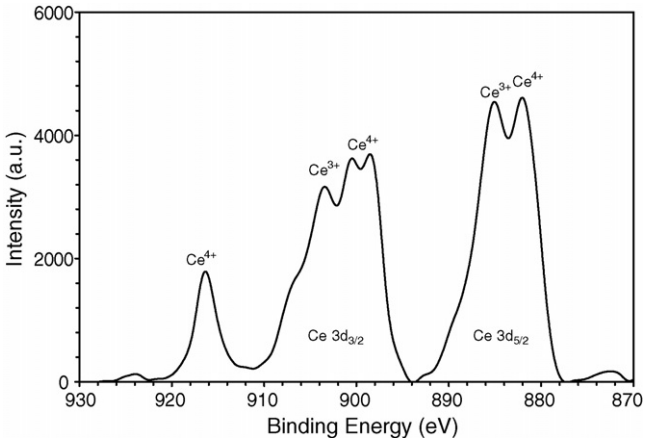

Fig. 3. Ce 3d XPS spectrum of synthesized Cerium oxide nanoparticles showing the presence of both Ce^{3+} and Ce^{4+} valence states.

The Ce^{3+} ions present in the nanocrystalline ceria can be converted to Ce^{4+} by hydroxyl free radicals in the hydrogen peroxide solution to give an electrochemical signal. But due to various surface chemical reactions the Ce^{4+} ions again go back to Ce^{3+} valence state. Following reactions are used to describe the chemistry of hydrogen peroxide with cerium oxide nanoparticles:

$$2Ce^{3+} + 2OH^- + H_2O_2 \rightarrow 2Ce(OH)_2{}^{2+} \quad (1)$$

$$Ce(OH)_2{}^{2+} + 2OH^- \rightarrow CeO_2 + 2H_2O \quad (2)$$

5. Sensor design and fabrication

A 3-terminal amperometric sensor consisting of a cerium oxide covered working electrode, an Ag/AgCl reference elec-