Electrochimica Acta 54 (2009) 6312–6321

Contents lists available at ScienceDirect

Electrochimica Acta

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

Amperometric detection of hydrogen peroxide at nano-nickel oxide/thionine and celestine blue nanocomposite-modified glassy carbon electrodes

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ARTICLE INFO

Article history:
Received 13 January 2009
Received in revised form 24 May 2009
Accepted 24 May 2009
Available online 6 June 2009

Keywords:
Thionine
Celestine blue
Nickel oxide
Nanoparticles
Modified electrode
H_2O_2 detection

ABSTRACT

A simple procedure was developed to prepare a glassy carbon (GC) electrode modified with nickel oxide (NiOx) nanoparticles and water-soluble dyes. By immersing the GC/NiOx modified electrode into thionine (TH) or celestine blue (CB) solutions for a short period of time (5–120 s), a thin film of the proposed molecules was immobilized onto the electrode surface. The modified electrodes showed stable and a well-defined redox couples at a wide pH range (2–12), with surface confined characteristics. In comparison to usual methods for the immobilization of dye molecules, such as electropolymerization or adsorption on the surface of preanodized electrodes, the electrochemical reversibility and stability of these modified electrodes have been improved. The surface coverage and heterogeneous electron transfer rate constants (k_s) of thionin and celestin blue immobilized on a NiOx-GC electrode were approximately 3.5×10^{-10} mol cm^{-2}, 6.12 s^{-1}, 5.9×10^{-10} mol cm^{-2} and 6.58 s^{-1}, respectively. The results clearly show the high loading ability of the NiOx nanoparticles and great facilitation of the electron transfer between the immobilized TH, CB and NiOx nanoparticles. The modified electrodes show excellent electrocatalytic activity toward hydrogen peroxide reduction at a reduced overpotential. The catalytic rate constants for hydrogen peroxide reduction at GC/NiOx/CB and GC/NiOx/TH were $7.96 (\pm 0.2) \times 10^3$ M^{-1} s^{-1} and $5.5 (\pm 0.2) \times 10^3$ M^{-1} s^{-1}, respectively. The detection limit, sensitivity and linear concentration range for hydrogen peroxide detection were 1.67 μM, 4.14 nA μM^{-1} nA μM^{-1} and 5 μM to 20 mM, and 0.36 μM, 7.62 nA μM^{-1}, and 1 μM to 10 mM for the GC/NiOx/TH and GC/NiOx/CB modified electrodes, respectively. Compared to other modified electrodes, these modified electrodes have many advantages, such as remarkable catalytic activity, good reproducibility, simple preparation procedures and long-term stabilities of signal responses during hydrogen peroxide reduction.

1. Introduction

Metal oxide, oxyhydroxide and their relevant metal alloys are extensively used in many different areas, such as corrosion protective coatings, electrochemical capacitors, the electronic industry, magnetic nanostructures, photochemical energy conversion, lithium ion batteries and display technology [1–5]. Moreover, metal oxide films are the most interesting class of materials in electrocatalysis and pH sensing [6,7]. Many of the metal oxides are indirect band-gap semiconductors with electrical and optical properties that are exploited for many different applications, such as oxygen storage, electrochemical capacitors and super capacitors [8], transparent conducting electrodes [9], electrochromic materials [10] and semiconductor photoelectrodes [11]. In addition, due to the low production cost, high stability, good electrical properties, low resistivity, and remarkable redox properties of metal oxide particles and nanoparticles, they are suitable compounds for the fabrication of gas sensors [12], lithium ion batteries and storage materials [13]. Furthermore, metal oxide particles or nanoparticles are suitable matrices and novel candidates for the immobilization of different redox molecules and biomolecules due to their high electrical conductivity, high surface area, wide electrochemical working window, excellent substrate adhesion and stable chemical, electrochemical and physical properties. The electrocatalytic activity of different electron transfer mediators, when immobilized onto metal oxide films, is a new challenge in sensor fabrication and electrode modification technologies [14,15].

Due to the high electron transfer efficiency and low cost of water-soluble dyes, they have been used as redox mediators in electrocatalytic processes [16–19]. Since the dye molecules will pollute the reference and counter electrodes, it is not convenient to add them as electron transfer mediators to the sample solution. Therefore, it would be preferable to immobilize the dye molecules on the electrode surface. Several water-soluble redox dyes, such as methylene blue [20], methylene green [21], meldola blue [22], azure-I

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doi:10.1016/j.electacta.2009.05.078

and B [23,24], orthophenylendimines, [25], neutral red [26], toluidine blue [27] and other azine compounds [28], can be used as electron transfer mediators when immobilized on the electrode surface. Immobilization of electron transfer mediators to electrode surfaces is a key step for the design, fabrication and performance of the sensors and biosensors.

The conventional methods for immobilization of electron transfer mediators are physical adsorption, electropolymerization, covalent attachment, cross-linking and entrapment in a carbon paste matrix [29–34,20]. Although different modified electrodes have been prepared with redox dye molecules, most of these electrodes present quasi-reversible electrochemical behavior and even ill-defined cyclic voltammograms with large background currents. Therefore, the immobilization of different electroactive dye molecules on the surface of various electrode materials is receiving increasing interest in the field of chemically modified electrodes, electrocatalysis and electroanalysis. Different nanomaterials, such as carbon nanotubes, gold nanoparticles and carbon nanofibers, have been successfully used for the immobilization of thionine on electrode surfaces [35–37]. The prepared nanocomposites have been used as sensitive sensors and biosensors for the detection of fetoprotein [36], glucose [35] and ethanol [37]. Recently, we fabricated highly sensitive glucose biosensors based on the immobilization of thionine and celestine blue onto a carbon nanotube-modified glassy carbon electrode [38–40].

Metal oxide materials with micro- or nanostructure are promising candidate for immobilization substances because of their significant mechanical strength, high surface area, excellent chemical stability, and high ability for immobilization of different electron transfer mediators. Sensitive sensors and biosensors for hydrogen peroxide detection have been fabricated with immobilizing thionine, methylene blue, meldola blue, natural red and tolidine blue, onto titanium oxide nanoparticles [41,42], manganeous oxide [43] and niobium oxide [44,45].

Nickel oxide (NiOx) nanoparticles have received considerable attention in recent years due to their catalytic, optical, electronic and magnetic properties [46,47]. Because of the volume, quantum size, surface and macroscopic quantum tunnel effects, nanocrystalline NiOx is expected to possess even better properties than those of micrometer-sized NiOx particles [48–51]. Based on the unique properties of NiOx nanoparticles, they can be used for the immobilization of different molecules. The easy preparation, electroinactivity in physiological pH solutions and high porosity are advantages of nickel oxide nanomaterials for the entrapment of electron transfer mediators. Recently, we successfully used NiOx nanoparticles for the immobilization of biomolecules and their applications as sensors and biosensors for hydrogen peroxide and glucose detection [52–54]. In the present study, NiOx nanostructures were used for the immobilization of thionine and celestine blue. The prepared nanocomposite has been used as an excellent catalyst for H_2O_2 reduction at lower overpotentials. Cyclic voltammetry and amperometry have been used for the investigation of the electrochemical properties and electrocatalytic activity of the nanocomposite-modified electrode. The fabricated sensor was used for the detection of micromolar or even lowers concentrations of H_2O_2 at physiological pH, using hydrodynamic amperometry.

2. Experimental

2.1. Chemicals and reagents

The chloride salts of celestine blue ($C_{17}H_{18}ClN_3O_4$) and thionin acetate (3,7-diamino-5-phenothiazinium acetate) were obtained from Aldrich and used as received. H_2O_2 (30%, w/w) was obtained from Merck, and its diluted solution was prepared daily. $Ni(NO_3)_2$ and other reagents were of analytical reagent grade from Merck. Phosphate buffer solutions (PBS) (0.1 M) were prepared from H_3PO_4, KH_2PO_4 and K_2HPO_4 and the pH values were regulated with HCl and KOH solutions. Solutions were deaerated by bubbling high purity (99.99%) argon gas through them prior to the experiments. All electrochemical experiments were carried out at a temperature of $25 \pm 0.1\,^{\circ}C$.

2.2. Apparatus and procedures

Electrochemical experiments were performed with a computer-controlled μ-Autolab modular electrochemical system (Eco Chemie Ultecht, The Netherlands), driven with GPES software (Eco Chemie). A conventional three-electrode cell was used with a Ag/AgCl/(sat KCl) reference electrode, a Pt wire as the counter electrode and a glassy carbon disk (modified and unmodified) as the working electrode. Voltammetry on electrodes coated with thionine or celestine blue nano-NiOx modified electrodes was carried out in buffers free of dye molecules.

2.3. Modification of GC and GC/NiOx electrodes with thionine and celestine blue

The glassy carbon electrode (2 mm diameter) was carefully polished with alumina powder (1 and 0.05 μm) on polishing cloth. The electrode was placed in ethanol and sonicated to remove adsorbed alumina particles. The electrodeposition of metallic nickel was carried out using cyclic potential (20 scans between 0 and −1.0 V at a scan rate of $50\,mV\,s^{-1}$) in acetate buffer solution, pH 4, in a solution containing 1 mM nickel nitrate. The potential was repetitively cycled (30 scans) from 0 to 1 V at a scan rate of $100\,mV\,s^{-1}$ in fresh phosphate solution for the electrodissolution and passivation of a nickel oxide layer at a GC electrode [55]. An stable thin film of the dye molecules adsorbed on the electrode surfaces by immersing the GC/NiOx modified electrode in fresh buffer solution (pH 7) containing 5 mM celestin blue or thionine, for 5–120 s. The effective surface area of the electrode modified with nickel oxide nanoparticles was determined to be $0.12\,cm^2$ from the cyclic voltammogram of 1 mM $K_3[Fe(CN)_6]$ in buffer solution, pH 7. For the attachment of thionine or celestine blue on the surface of the GC electrode with electropolymerization, first, the glassy carbon electrode was carefully polished with alumina on a polishing cloth. Then, the potential of the electrode was maintained at 1.1 V vs. the reference electrode for 5 min in 0.1 M phosphate buffer solution. By cycling the potential between 0.1 and −0.5 V (30 cycles) at a scan rate of $100\,mV\,s^{-1}$, in pH 7 phosphate buffer solution (0.1 M) containing 0.1 mM thionine or celestine blue, a thin layer of the dye molecules was adsorbed [56]. For adsorption of thionine or celestine blue on the surface of the reactive GC electrode, the process was carried out in two steps. First, the glassy carbon electrode was held under a constant potential of 1.8 V for 20 min in 1 M sulfuric acid solution. Second, the preanodized GC electrode was immersed in 0.1 mM thionine or celestine blue solution for 1 h.

3. Results and discussion

3.1. Electrochemical properties of thionin and celestin blue modified electrodes

The formation and growth of electrodeposited nickel oxide nanoparticles on a glassy carbon electrode were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) (Fig. 1A–C). As shown, nickel oxide particles grow by electrodeposition on the amorphous glassy carbon surface. The average size of the NiOx particle varies from under 50 nm to slightly less than 200 nm. AFM images also show nickel oxide nanostructures