



An electrochemical acetylcholine sensor based on lichen-like nickel oxide nanostructure

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ABSTRACT

Lichen-like nickel oxide nanostructure was synthesized by a simple method and characterized. The nanostructure was then applied to modify a carbon paste electrode and for the fabrication of a sensor, and the electrocatalytic oxidation of acetylcholine (ACh) on the modified electrode was investigated. The electrocatalytic efficiency of the nickel oxide nanostructure was compared with nickel micro- and nanoparticles, and the lichen-like nickel oxide nanostructure showed the highest efficiency. The mechanism and kinetics of the electrooxidation process were investigated by cyclic voltammetry, steady-state polarization curve and chronoamperometry. The catalytic rate constant and the charge transfer coefficient of ACh electrooxidation by the active nickel species, and the diffusion coefficient of ACh were reported. A sensitive and time-saving hydrodynamic amperometry method was developed for the determination of ACh. ACh was determined with a sensitivity of $392.4 \text{ mA M}^{-1} \text{ cm}^{-2}$ and a limit of detection of $26.7 \text{ }\mu\text{M}$. The sensor had the advantages of simple fabrication method without using any enzyme or reagent and immobilization step, high electrocatalytic activity, very high sensitivity, long-term stability, and antifouling surface property toward ACh and its oxidation product.

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1. Introduction

Acetylcholine (ACh) is the most abundant excitatory neurotransmitter and can be found in both the central nervous system and the skeletal neuromuscular junctions (Sine, 2012). It plays signaling role in brain cholinergic system which affects attention, learning and memory, sleep, and arousal (John and Carolina, 2001). The accumulation of acetylcholine in the nervous tissue is actually the result of an inability to metabolize acetylcholine and according to the clinical explorations, the unstable regulation of ACh concentrations causes some neuropsychiatric disorders such as Parkinson's and Alzheimer's diseases, myasthenia gravis, progressive dementia and schizophrenia (Davis and Berger, 1979). Therefore, more sensitive and accurate measurement methods of ACh have received remarkable importance. Indeed, acetylcholine lacks electroreactive, chromophore or fluorophore groups. For this reason, many well-proven methods applied for other neural transmitters are unusable and its determination by

using extended methods generally needs a conversion into more easily detectable compounds. A variety of methods for the determination of ACh have been reported comprising matrix-assisted laser desorption ionization time-of-flight mass spectrometry (Persike et al., 2010), liquid chromatography coupled to post-column chemiluminescence detection (Yoshida et al., 2009), radioimmunoassay (Woodman et al., 1982), potentiometry (Barsoum et al., 2004), amperometric methods based on enzyme-modified surfaces (Shimomura et al., 2009), enzyme-based biosensors (Burmeister et al., 2008), gas chromatography–mass spectrometry and liquid chromatography coupled to post-column enzymatic detection (Tsai, 2000; De Bundel et al., 2008) and enzymatic electrochemical biosensors (Zhu et al., 2009; Gorski et al., 2009). Over the past decade, the development of electrochemical methods, especially nonenzymatic sensors, has risen at a considerable rate for detection of ACh (Shibli and Beenakumari, 2006; Shibli et al., 2006; Lin and Chou, 2005; Heli et al., 2009a, 2010).

Metal and metal oxides nanostructures have recently aroused tremendous interests in a broad range of fundamental studies and technological applications because of their significant size- and shape-dependent properties which differ from their bulk counterparts in attractive nanomorphologies, functional biocompatibility, enhanced electron-transfer kinetics, non-toxic properties and high

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biological activity leading to enhanced sensing characteristics (Heli et al., 2010, 2009a, 2012; Sattarahmady et al., 2010a, 2010b; Heli and Yadegari, 2010; Rodriguez and Fernandez-Garcia, 2007). Among nanostructured oxides of metals, nickel (hydr)oxide is a hole-type semiconductor with a wide band-gap energy range and possesses distinctive features of high specific capacitance, outstanding durability, chemical stability, large span optical density and catalytic and electrochemical activities (Sattarahmady et al., 2010a, 2010b; Lai et al., 2006; Niklasson and Granqvist, 2007; Barde et al., 2004; Ling and Hwang, 1998). Up to now, nickel oxide nanostructures have received continuous attention in electrochemical sensors and biosensors owing to high reactivity, environmental compatibility, low cost, and shape and size dependency of reactivity (Sattarahmady et al., 2010a, 2010b; Liu et al., 2009; Mu et al., 2011).

Flower-shape nanostructures have been synthesized in recent years via different methods of oxidation, reduction, decomposition and electrodeposition due to interesting structure, shape and properties and have potential applications in electrochemical, electrical, optical and magnetic devices (Kharisov, 2008; Heli et al., 2012; Ge et al., 2012; Cao et al., 2011). These applications are due to low density, large active surface area, and surface permeability of these nanostructures.

In the present study, lichen-like nickel oxide nanostructure was synthesized and characterized. The nickel oxide nanostructure was then employed to modify a carbon paste electrode; the electrochemical kinetics of the resultant electrode was studied and finally applied to the electrocatalytic oxidation and determination of ACh.

2. Experimental

Nickel microparticles with the diameter of $< 10 \mu\text{m}$ were obtained from Sima Felez, Co., Iran. Graphite fine powder with a particle size of $< 50 \mu\text{m}$ was obtained from Merck. All other chemicals used in the experiments were of analytical grade from Merck or Sigma and were used without further purification. All solutions were prepared with doubly distilled water.

Nickel nanoparticles were synthesized by a polyol method in the presence of polyvinylpyrrolidone (PVP) as the capping agent (Jin et al., 2006). In a typical synthesis, a given amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1% PVP was dissolved in water. 1.0 M NaOH solution was then added to adjust the solution pH to 11. The mixture was stirred for 2 h at 60°C . Then, the resultant $\text{Ni}(\text{OH})_2$ slurry was filtered and washed. The obtained $\text{Ni}(\text{OH})_2$ slurry, 3.0 g NaOH, 0.4 g PVP, and 100 mL ethylene glycol were added to a flask and stirred. The mixture was then refluxed for 4 h at 180°C . The product was filtered and washed with distilled water and ethanol. The product, gray to black nickel nanoparticles, was finally dried at ambient temperature.

Lichen-like nickel oxide sample was synthesized by a desolvation method. In a typical synthesis, 291 mg $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was firstly dissolved in 10 mL water. Concentrated ammonia solution was then added until $\text{Ni}(\text{OH})_2$ precipitate formation. The precipitate color was light green. Addition of ammonia was continued just to dissolve this precipitate and complete the formation of soluble nickel–ammonia complex. The solution pH and color were ≈ 10 and dark blue, respectively. This solution was placed near another solution containing a hygroscopic material in a closed container for desolvation. The nickel–ammonia complex solution was practically placed near a beaker containing 10 mL concentrated sulfuric acid in a closed polyethylene container for 48 h at room temperature. After that time, a light green precipitate was obtained. The precipitate was washed with water and ethanol and dried at 40°C to obtain the nickel oxide nanostructure.

Electrochemical measurements were carried out in a conventional three-electrode cell containing 100 mM NaOH solution powered by a μ -Autolab type III potentiostat/galvanostat (The Netherlands). An Ag/AgCl, 3 M KCl, a platinum disk and a modified carbon paste electrode were used as the reference, counter and working electrodes, respectively. The system ran on a PC through GPES 4.9 software. The working electrodes were unmodified (UCPE) or modified carbon paste electrodes.

UCPE was prepared by hand-mixing graphite fine powder and mineral oil with a 80/20% (w/w) ratio. The paste was packed firmly into a cavity (2 mm diameter) at the end of a Teflon tube. Electrical contact was established by a copper wire.

Modified carbon paste electrodes with nickel microparticles, nickel nanoparticles, or lichen-like nickel oxide nanostructure (MCPE) were prepared by mixing graphite fine powder, mineral oil, and nickel-based materials with ratios of 60:20:20 by wt%. In order to cover the MCPE surface with a Nafion layer, 10 μL of a 2% w/v low aliphatic alcohols Nafion solution was dropped on the electrode surface and placed under an IR lamp to dry. Before performing any experiment, the modified carbon paste electrodes were transferred to the supporting electrolyte and 25 potential cycles were applied in a regime of cyclic voltammetry in the potential range of -200 – 800 mV at a potential sweep rate of 50 mV s^{-1} . This procedure caused the voltammograms of MCPE to become more stable and reproducible, or transformation of nickel (micro- and nano-) particles to the corresponding nickel oxide.

In order to compare the electrocatalytic activities of the modified electrodes toward the electrooxidation of ACh, the currents in the voltammograms were normalized with respect to the effective surface area. To obtain such effective surface areas, the anodic charges passed for the oxidation of nickel species in the supporting electrolyte were measured (0.0141, 0.080, 0.088 cm^2 for nickel microparticles, nickel nanoparticles and lichen-like nickel oxide nanostructure-modified electrodes, respectively) and were related directly to the effective surface areas.

In order to obtain information about the morphology and size of the nanostructure, scanning electron microscopy (SEM) was performed using a X-30 Philips instrument.

All measurements were carried out at room temperature.

3. Results and discussion

SEM micrographs of the nickel oxide sample with different magnifications are shown in Fig. 1. The micrograph shows lichen-like microstructure comprising calycles of ≈ 30 nm-thickness nanoflakes. The nanoflakes were irregular and collected together. The sample is highly porous and alveolar with a high effective surface area and aspect ratio through which an electrolyte can easily permeate into the nanostructure.

Fig. 2A, inset represents typical cyclic voltammogram of MCPE in the running electrolyte recorded with a potential sweep rate of 50 mV s^{-1} . MCPE exhibits a pair of well-defined peak in the voltammogram. The formal potential of the couple is 400 mV as mid peak ($E^0 = (E_{p,a} + E_{p,c})/2$), which is derived from cyclic voltammograms recorded at slow potential sweep rates of $< 10 \text{ mV s}^{-1}$. In the voltammogram, the ratio of the peak currents (I_{pa}/I_{pc}) is almost equal to unity and the pattern of the voltammogram is similar to those previously reported (Hajjizadeh et al., 2008; Sattarahmady et al., 2010a, 2010b). The involved redox transition is attributed to the Ni(II)/Ni(III) species immobilized at the MCPE surface via the following reaction (Hajjizadeh et al., 2008; Sattarahmady et al., 2010a, 2010b; Heli et al., 2009b):



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