



Preparation of perovskite-type composite oxide $\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3\text{-NiFe}_2\text{O}_4$ and its application in glucose biosensor

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ABSTRACT

A novel nanostructured perovskite-type composite oxide $\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3\text{-NiFe}_2\text{O}_4$ (LNT-NFO) was synthesized by sol-gel method and characterized by X-ray diffractometer (XRD) and transmission electron microscopy (TEM). Amperometric glucose biosensors based on the carbon paste electrode (CPE) were constructed by immobilizing glucose oxidase (GOD) with LNT-NFO and the experimental conditions such as the amount of GOD, pH value, and applied potential were investigated. Under the optimum conditions, the electrochemical performances of the LNT-NFO with different ratios of LNT-NFO (10:1, 20:1, 30:1) modified CPE have been researched on the oxidation of glucose. The results show that LNT-NFO (20:1) can immobilize GOD more effectively. The biosensor based on LNT-NFO/CS/GOD modified CPE exhibits good reproducibility, stability and selectivity in glucose determination with linear signal-to-glucose concentration range of 0.5–10 mM and a detection limit ($S/N = 3$) of 0.04 mM.

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1. Introduction

The perovskite oxide ABO_3 is frequently encountered structure in inorganic chemistry, and this structure can accommodate most of the metallic ions in the periodic table with a significant number of different anions. Some properties such as photocatalytic property [1,2], magnetic properties [3,4], conductivity and dielectric property [5] have been widely investigated. As an attractive material, perovskite oxide had been used in the areas of electrochemical gas sensors, solid fuel cells and lots of oxidation and reduction catalytic processes which has been reviewed thoroughly [6,7]. The perovskite-type titanium oxide denoted as RTiO_3 , where counter cation of R is La or Y, has the GdFeO_3 -type distorted orthorhombic structure [8]. Y can be partially substituted, leading to a wide variety of mixed oxides with more and more unique properties like the application of NO_x removal [9]. In recent years, being a famous catalyst, inorganic perovskite nano-materials have been received more and more attention in the area of chemical modified electrode. For example, Anh et al. [10] have reported that the catalytic properties of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ for hydrogen peroxide decomposition depends on the oxygen vacancies and proposed the use of this material deposited on a Pt electrode for the determination of hydrogen peroxide. Chen et al. [11] have synthesized perovskite structure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sub-microspheres to fabricate electrochemical

sensor with hemoglobin to detect hydrogen peroxide which displayed very good performance. Luque et al. [12] have reported the catalytic property of manganese based perovskites-type oxides for oxidation and reduction toward hydrogen peroxide is highly dependent on the nature of the A cation and on the temperature and time of calcination employed during the synthesis. However, there are few detailed reports for the glucose detection by electrochemical sensor based on perovskite modified electrode with glucose oxidase (GOD).

As we all know, Glucose is an important metabolite for living organisms, especially for clinical diagnostics of diabetes, which is a world-wide public health problem and one of the leading causes of death and disability in the world. Therefore, the estimation of glucose in blood is quite an important parameter. Since the first enzyme electrode was reported by Clark and Lyons [13], many researches have been carried out to study the enzyme-based glucose biosensors, especially amperometric biosensors [14]. It has been found that GOD, containing a flavin adenine dinucleotide (FAD) redox center that catalyzes the electron transfer from glucose to gluconolactone, has been extensively used to monitor the glucose in biochemistry, clinical chemistry, food processing and fermentation [15], and bioelectrocatalysis based on direct and mediated electrochemistry of GOD can also be used to detect and determine glucose, thus establishing the foundation of electrochemical biosensor. At the beginning, the detection of glucose by electrochemical biosensors is based on the electrochemical oxidation of hydrogen peroxide generated by enzyme-catalyzed oxidation of glucose at anodic potentials [16,17] which

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belongs to the first-generation biosensor. However, it is well known that the active redox center of GOD, FAD is deeply buried by the protective protein shell, which makes the direct electron transfer from the redox center of GOD to the electrode surface extremely difficult [18], so the ferrocene derivatives [19–23] and tetrathiafulvalene derivatives [24] as redox mediators received considerable attention. At the same time, the immobilization of GOD on the electrode surface which is one of the main factors that affect the performance of a glucose electrochemical biosensor has attracted more and more people. Until now, various materials have been utilized to immobilize the GOD such as metal nano-material [25,26], carbon nanotube [27], organic polymer [28], hydrotalcite [29], and spinel [30].

In this paper, a series of perovskite-type composite oxides $\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3\text{-NiFe}_2\text{O}_4$ (LNT–NFO) with different ratios of $\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (LNT) to NiFe_2O_4 (NFO) (10:1, 20:1, 30:1 (w/w)) were synthesized by sol–gel method, and used to modify CPE with GOD to build a mediated electrochemical glucose biosensor. The electrochemical performance of the modified electrode was investigated by cyclic voltammetry and amperometry. To the best of our knowledge, CPE modified with this new material immobilizing GOD for the development of amperometric glucose biosensors has not been reported so far.

2. Experiments

2.1. Apparatus and reagents

A CHI660C electrochemical workstation (Shanghai Chenhua Co. Ltd., China) controlled by a microcomputer with CHI660C software was employed for all electrochemical measurements in the experiment. The three-electrode system consisted of modified CPE working electrode, platinum wire auxiliary electrode and a saturated calomel reference electrode.

Characterization of the synthesized samples LNT, NFO and LNT–NFO: Powder X-ray diffraction (XRD) patterns were obtained on Rigaku DLMAX-2200 X-ray diffractometer using $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA; scanning rate: $0.08^\circ \text{ s}^{-1}$) in range $2\theta = 20\text{--}90^\circ$. Transmission electron microscopy (TEM) of LNT–NFO was obtained by a TEM (JEOL JEM-200CX working at 160 kV) instrument.

GOD (EC 232-601-0, type VII, from *Aspergillus niger*, 197,000 units/G), ferrocenecarboxylic acid (Fca) were purchased from Sigma–Aldrich. Chitosan (CS), β -D-glucose, graphite powder (spectral reagent), paraffin oil, Na_2HPO_4 , NaH_2PO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, NaOH, HNO_3 , $\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ and $\text{C}_2\text{H}_5\text{OH}$ were purchased from the Sinopharm Group Chemical Reagent Co., Ltd. All reagents were of analytical reagent grade. All solutions were prepared with redistilled water. The phosphate buffer solution (PBS, 0.1 M) was chosen as the supporting electrolyte.

2.2. Synthesis of LNT–NFO nanoparticles

NFO was synthesized according to the Ref. [31]. The method of sol–gel was used to synthesize a series of the perovskite and related compounds LNT and LNT–NFO. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2:1, molar ratio) were dissolved in the appropriate HNO_3 solution, and the citric acid (0.15 mol) was dropped into the mixture. The mixed solution was heated at 363 K in the water bath after the final pH value was 2–3 adjusted by $\text{NH}_3 \cdot \text{H}_2\text{O}$ until the colloidal sol came into being. Another mixed ethanol solution of tetrabutyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}:\text{C}_2\text{H}_5\text{OH} = 1:17$, v/v) with different ratio of $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ to NFO (10:1, 20:1 and 30:1, w/w) was transferred into the colloidal sol, agitated violently for

1 h after ultrasound for 30 min, and then the sol–gel was calcined for 1 h at 673 K, and 3 h at 1073 K.

2.3. Preparation of the GOD biosensor

Graphite powder and paraffin oil with the proportion of 2:1 (w/w) were mixed in the agate mortar for 20 min. The mixture was firmly packed into the glass tube ($\phi = 3.0 \text{ mm}$) which had been ultrasonicated in HNO_3 , NaOH solution and redistilled water in turns, and then the copper wire was inserted from another end of the tube. The CPE was polished with a piece of weighing paper and rinsed thoroughly with redistilled water.

GOD biosensor was fabricated as follows: 250 μL 0.5 wt.% CS was fully mixed with 1.5 mg LNT–NFO and 1.25 mL redistilled water with ultrasonic agitation over 2 h, and then 1 mg GOD was added to appropriate amount of the mixture to be ultrasonicated 5 min. At last, 9 μL of the resulting homogeneous solution was spread evenly onto the well-polished CPE surface with a syringe and allowed to dry overnight to form a LNT–NFO/CS/GOD enzyme-incorporated composite film at 4°C . The electrode was washed by redistilled water and stored at 4°C when it was not used.

2.4. Procedure of glucose measurement

All electrochemical experiments were carried out in 10 mL of 0.1 M PBS containing 0.5 mM Fca. Oxidation of glucose on the LNT–NFO/CS/GOD/CPE was monitored using amperometric current–time (I – t) curve by measuring the increase of generated current during successive addition of glucose standard solution to the solution under stirring condition. Cyclic voltammograms (CVs) were obtained by scanning the potential between -0.4 and 0.8 V (scan rate: 100 mV/s).

3. Results and discussion

3.1. Characterization of the synthesized samples

Fig. 1 shows the XRD patterns of the synthesized samples. As is shown that the characteristic reflections of (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), (2 2 1) and (3 1 0) at ca. $2\theta = 23^\circ$, 32° , 40° , 47° , 52° , 58° , 68° , 72° , and 77° matched well with the standard XRD pattern of LaTiO_3 (JCPDS file 75-0267) and hence confirmed the formation of LaTiO_3 . At the same time, some peaks appeared at ca. $2\theta = 32^\circ$, 40° , 47° , and 58° attributed to the charac-

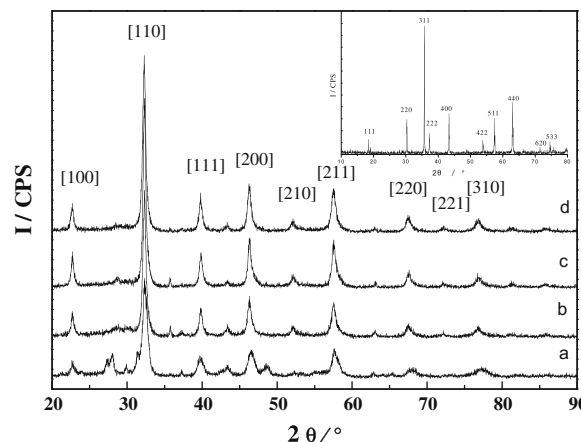


Fig. 1. Xrd patterns of LaNiTO_3 (a), $\text{LaNiTO}_3\text{-NiFe}_2\text{O}_4$ (LNT–NFO) with the ratio (LNT:NFO) of 10:1 (b), 20:1 (c), 30:1 (d). Insert: XRD patterns of NiFe_2O_4 .

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