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Non-enzymatic amperometric glucose biosensor based on nickel hexacyanoferrate nanoparticle film modified electrodes

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ABSTRACT

A non-enzymatic amperometric glucose biosensor based on the modification of functional nickel hexacyanoferrate nanoparticles was prepared via electrochemical deposition. The electrochemical deposition of the nickel hexacyanoferrate nanoparticles was obtained by potential cycling in a solution containing nickel (II) and hexacyanoferrate (III) producing a modified surface with a high degree of uniformity. The modified electrode is exemplified towards the non-enzymatic sensing of glucose where using cyclic voltammetry and amperometry, low micro-molar up to milli-molar glucose concentrations are readily detectable. The non-enzymatic sensing of glucose also shows a modest selectivity over ascorbic acid. This platform offers a novel route for glucose sensors with wide analytical applications.

1. Introduction

The development and fabrication of cost-effective, simple, accurate, portable and rapid sensors for glucose are socially important aiding diabetics globally which represents roughly 5% of the world's population [1]. Certain areas of medical, food and environmental analysis require rapid and inexpensive monitoring methods for glucose in blood and food [2,3]. The measurement of glucose concentration in blood is critical for diagnosis of diabetes mellitus in order to avoid some of the long-term diabetic syndromes such as retinal and kidney damage [4,5].

In responses to the needs for frequent or continuous monitoring of glucose in diabetes there is a need for the development of improved sensors [6]. Nowadays the pursuit of non-enzymatic glucose sensing with rapid response and precise measurement is a vigorous and competitive area of research. The direct oxidation of glucose by different electrodes in the absence of enzyme has been studied [7–12]. Various metal electrodes such as Pt, Au, and Ag have been proved to be highly electro-active in the anodic oxidation of glucose requiring a high overpotential. However, these can be problematic due to poisoning/fouling of the electrode surface, especially at gold and platinum electrodes. Additionally the cost of these precious metals needs to be considered. As a consequence, there are increasing interests on the fabrication of modified electrodes with low operating potential by enhancing electron transfer kinetics. In comparison, a few transition metal complexes, including the various transition metal hexacyanoferrate modified electrodes, have been shown to be efficient electro-catalysts for anodic oxidation of glucose, giving enhanced stability towards the target analyte, with low detection limits and wide analytical ranges achievable [13–18]. In this area problems from the instability of modified electrodes are evident and limit widespread implementation.

Consequently in this paper, we describe a simple route to the production of uniform functional nickel hexacyanoferrate nanoparticles using electrochemical deposition. The preparation method is simple and nickel hexacyanoferrate nanoparticles may be readily formed on a glassy carbon electrode surface constructing a simple, economical and accurate amperometric sensor for glucose. The non-enzymatic glucose biosensor based on nickel hexacyanoferrate (NiHCF) modified electrodes provides a prominent augmentation of response current toward glucose with a good stability and reproducibility.

2. Experimental

2.1. Chemical reagents

All chemicals were of analytical grade from Changzheng (Chengdu, China) and were used without further purification. All

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solutions were prepared with double distilled water, and degassed with oxygen free nitrogen. All experiments were carried out at a temperature of 295 ± 3 K.

2.2. Instrumental

Electrochemical measurements were performed using a LK9805 electrochemical analyzer (Tianjin, China). A glassy carbon electrode (GCE) was used as working electrode with a bright platinum foil as a counter electrode and a Ag/AgCl reference electrode completing the circuit. Scanning electron micrographs (SEM) were obtained with a scanning electron microscope (SEM, Hitachi S-800, 20 kV).

2.3. Preparation of the modified electrode

Electro-deposition was performed using solutions containing 0.05 M KCl, 0.5 mM $K_3[Fe(CN)_6]$ and 1.2 mM $NiCl_2$. Unless otherwise stated, the procedure involved 25 full voltammetric cycles at 50 mV s^{-1} in a potential range from −0.1 to 1.0 V. NiHCF film was fabricated on GCE substrates with a diameter 5 mm. Prior to the film deposition, the GCE was polished on alumina lapping compounds (BDH) of decreasing sizes (5–0.1 μm) on soft lapping pads.

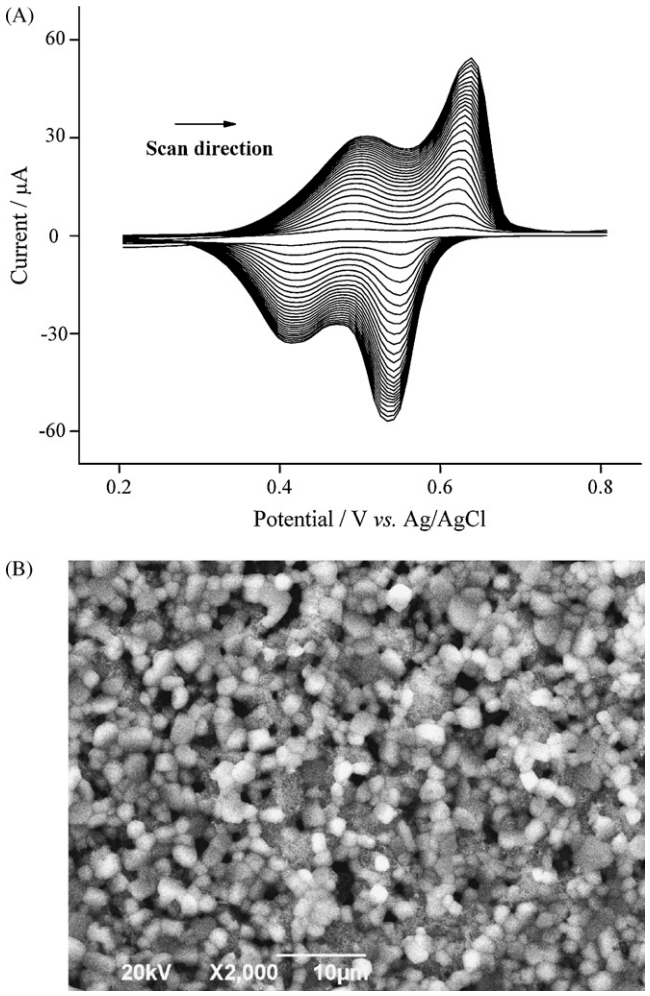

Fig. 1. (A) Cyclic voltammograms (25 cycles) of NiHCF films at the glassy carbon electrode recorded in 0.5 mM $K_3[Fe(CN)_6]$ + 0.05 M KCl + 1.2 mM $NiCl_2$ solutions with Ag/AgCl reference electrode. Scan rate: 50 mV s^{-1}. (B) SEM images of the NiHCF film.

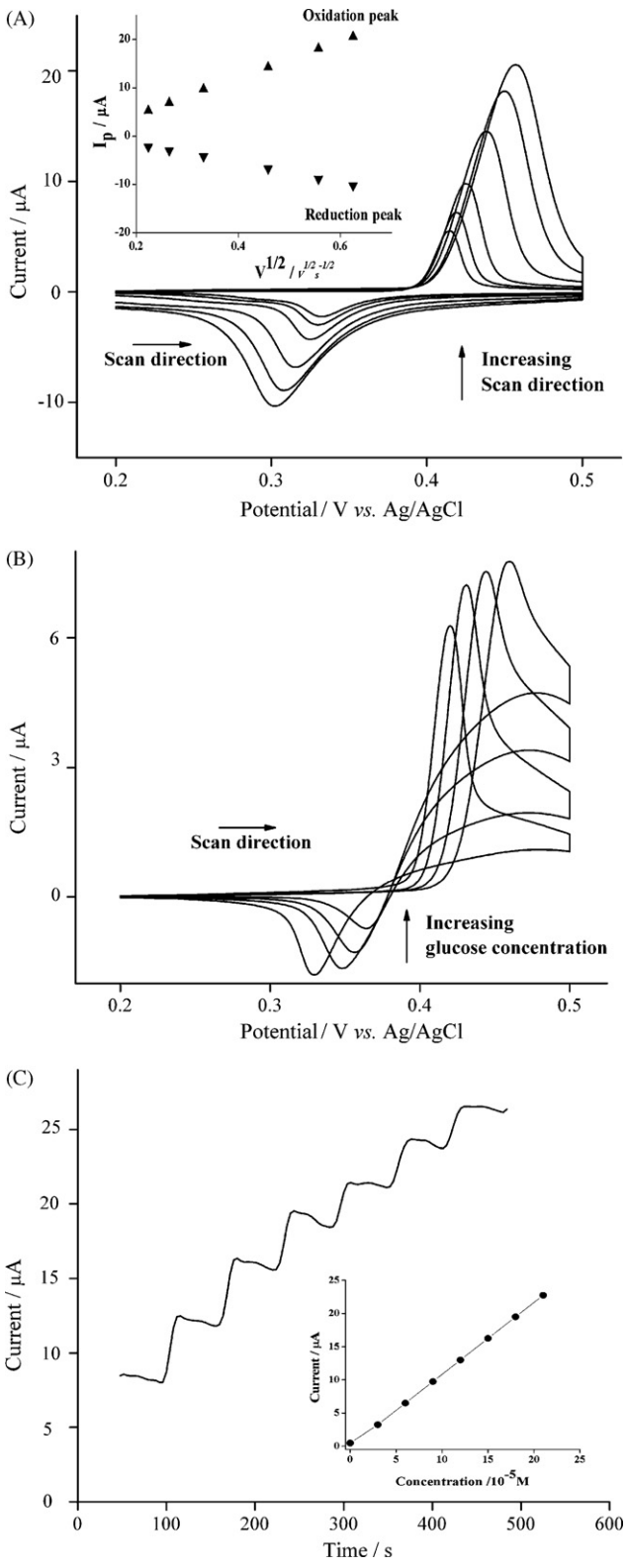

Fig. 2. (A) Cyclic voltammetric responses of NiHCF modified electrodes at various scan rates from 50 to 500 mV s^{-1} in 0.5 M NaOH solution. Inset: The plot of the oxidation peak currents and the reduction currents for NiHCF modified electrodes against the square root of scan rates. (B) Electrochemical responses of NiHCF modified electrodes to glucose in 0.5 M NaOH solution: (a) without glucose (b) 2 mM glucose (c) 4 mM glucose (d) 8 mM glucose. Scan rate: 50 mV s^{-1}. (C) Amperometric responses of NiHCF modified GCE to increasing the glucose concentration with applied potential 0.5 V vs. Ag/AgCl; Insert: Corresponding calibration curve at NiCHF modified glucose biosensor.

Table 1
Reproducibility of the NiHCF modified electrodes*.

Times	1	2	3	4	5	6	7	8	9	10	R.S.D = 1.9%
$i/10^{-6}$ A	8.79	8.78	8.67	8.59	8.47	8.62	8.39	8.71	8.35	8.36	

* Measure conditions: 0.5 M NaOH solution containing 0.2 mM glucose.

3. Results and discussion

3.1. Preparation and characterization of NiHCF particles on GCE

The nickel hexacyanoferrate (NiHCF) particles were electrochemically deposited on the surface of GCE which involved 25 full voltammetric cycles over the potential range −0.1 to +1.0 V vs. Ag/AgCl at a scan rate of 50 mV s^{-1} in an aqueous solution containing 0.05 M KCl, 0.5 mM $K_3[Fe(CN)_6]$ and 1.2 mM $NiCl_2$. Fig. 1A shows voltammetric data illustrating the growth of NiHCF films during potential cycling. Under such conditions, first the reduction of hexacyanoferrate (III) proceeds during negative potential scans, and hexacyanoferrate (II) ions are generated in the vicinity of the electrode surface where they react primarily with Ni(II). The relative electrochemical processes are attributed to [19]:

$$Fe(CN)_6^{3-} + e \rightleftarrows Fe(CN)_6^{4-} \quad (1)$$

$$2K^+ + Fe(CN)_6^{4-} + Ni^{2+} \rightleftarrows K_2Ni^{II}\left[Fe^{II}(CN)_6\right] \quad (2)$$

$$K_2Ni^{II}\left[Fe^{II}(CN)_6\right] \rightleftarrows KNi^{II}\left[Fe^{III}(CN)_6\right] + e + K^+ \quad (3)$$

The morphology and grain sizes of NiHCF formed on electrode (GCE) were examined using SEM shown in Fig. 1B. It was found that the obtained NiHCF film is actually composed of well-dispersed spherical particles with diameters in the range 300–1500 nm. Also note that the surface is uniform and compact with the electrode surface covered with highly dispersed particles, indicating an effective modification of the GCE via electrochemical deposition which provide a large active surface area.

In order to gain a further understanding of the electrochemical properties of the modified film, NiHCF particles were explored in sodium hydroxide solutions via potential cycling. Fig. 2A shows cyclic voltammograms at various scan rates obtained at the NiHCF/GCE electrode in a 0.5 M NaOH solution. The redox transitions involved are attributed to the redox reactions of surface-confined Ni^{2+}/Ni^{3+} as follows [20]:

$$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + e + H_2O \quad (4)$$

The plot of the reduction peak currents against the square root of scan rate (50–500 mV s^{-1}) shows an excellent linear direct relationship, which suggests that the electrochemical process is a diffusion-controlled electron transfer process rather than surface-controlled at these scan rates. Observation of the peak-to-peak separation as a function of scan rates indicates a quasi-electron transfer kinetics. It is clear that nickel (II) hexacyanoferrate can be considered as a model system since its 'film' on electrode surfaces are characterized by well-defined and reproducible responses in aqueous alkaline supporting electrolytes. NiHCF structures seem to be fairly open and permit unimpeded transport of alkali metal cations of different sizes while providing charge balance during the system's redox reaction. Thus NiHCF could also be a very good host matrix.

3.2. Electrochemical performances of glucose biosensors based on NiHCF modified GCE electrodes

The electrochemical oxidation of glucose was investigated in 0.5 M NaOH using the functionalized NiHCF via cyclic voltammetry. For clarity the voltammetric response in the absence of glucose was also recorded. The corresponding voltammograms are shown in Fig. 2B where is it clear that there is an apparent enhancement in the oxidation peak current as the concentrations of glucose is increased indicating that glucose has been oxidized by the active NiHCF particles via a cyclic mediation redox process. On the other hand, with the increase of glucose concentration, the oxidation current increased monotonously and the reduction current decreased accordingly with the following reactions [21]:

$$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e \quad (5)$$

$$Ni(OH) + \text{glucose} \rightarrow Ni(OH)_2 + \text{glucolactone} \quad (6)$$

Over the scan rates range from 50 to 4000 mV s^{-1} both the oxidation and reduction currents increase linearly with the square root of scan rate indicating that the electrochemical reactions are diffusion-controlled, which is ideal for the detection of glucose.

3.3. Performance of NiHCF/GCE biosensor to glucose detection

Amperometric glucose measurements were performed with the prepared biosensor at a fixed working potential in NaOH solution under continuous stirring. After stabilization of the baseline, glucose solution was injected and the plot of current versus time was recorded. Fig. 2C shows a typical response of the biosensor to the successive addition of glucose at working potential of 0.5 V vs. Ag/AgCl. The NiCHF/GCE biosensor exhibited well-defined current responses obtained at the biosensor. The response of the biosensor is very fast in reaching a dynamic equilibrium upon each addition of the sample solution, generating a steady-state current signal within 4 s. The lower inset shows the calibration curve for glucose concentrations with an excellent linear relationship range from 5×10^{-6} to 2.5×10^{-3} M against a correlation coefficient 0.999. The detection limit was estimated as (3 sigma) 1.25×10^{-6} M. This biosensor also presented good reproducibility for the detection of glucose. The repeatability of the biosensor, a 0.2 mM glucose solution was measured ten times and excellent relative standard deviation (R.S.D) of 1.9% was achieved shown in Tables 1 and 2 shows the fabrication repeatability of 10 biosensors with an acceptable relative standard deviation of 2.8%. Moreover, the long-term stability of the biosensor was also checked. After two weeks of continuous measurements, it still kept 93% of its response activity compared with its initial value. Also the interference of substances such as ascorbic acid was also explored. According to normal values (Physiological) [22], the concentration ratio of glucose to ascorbic acid is 10. The response current hardly had changes shown in Table 3. The results showed the good selectivity of the NiHCF modified biosensor towards the detection of glucose. An important note to electro-analysts is that

Table 2
The fabrication repeatability of the NiHCF modified electrodes*.

Times	1	2	3	4	5	6	7	8	9	10	R.S.D = 2.8%
$i/10^{-6}$ A	8.30	8.87	8.43	8.79	8.46	8.85	8.36	8.89	8.31	8.50	

* Measure conditions: 0.5 M NaOH solution containing 0.2 mM glucose.

Table 3
The influence of ascorbic acid on the response of glucose*.

Interference substance	Physiological concentration (mM)	I_{G+A}/I_G
Ascorbic acid	0.1	1.007

* I_G, the current response of 1.0 mM glucose; I_{G+A}, the current response of 1.0 mM glucose in the presence of 0.1 mM.

the careful choice of underlying electrode needs to be made when fabricating this electrode. In our case the electrochemical oxidation of ascorbic acid occurs at less positive potentials than the analytical peak of interest and is suitably (voltammetrically) separated and has no effect on analytical sensing protocol. It has been elegantly demonstrated [23] that the electrochemical oxidation of ascorbic acid depends on the heterogeneity of the electrode surface. In our case an underlying glassy carbon is used to support the electro-catalytic NiHCF particles and the heterogeneity, that is, the proportion of edge plane like-sites/defects is high compared to the proportion of basal plane like-sites/defects ensuring that the electrochemical oxidation of ascorbic acid occurs at a facile potential. As the heterogeneity of glassy carbon can change depending on its grade, a poor choice may result in an electrode with a high proportion of basal plane sites compared to edge plane sites and in that case, the electrochemical oxidation of ascorbic acid will occur at higher oxidation potentials close of the electro-activity of the NiHCF and detrimentally affecting its sensing.

4. Conclusion

We have developed a simple method to prepare a NiHCF/GCE biosensor. The resulting functional NiHCF film was characterized by SEM and cyclic voltammetry. The electrode modified with the NiHCF film showed a higher electro-catalytic activity and stability for glucose. It was found that NiHCF could strongly enhance the electrode transfer and possess excellent electro-catalytic property to glucose. A glucose biosensor based on NiHCF/GCE was successfully fabricated and demonstrated for sensitive and selective detection of glucose with excellent performances towards glucose sensing in the absence of enzyme.

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