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Fabrication of a glucose sensor based on a novel nanocomposite electrode

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ABSTRACT

The direct electrocatalytic oxidation of glucose in alkaline medium at nanoscale nickel hydroxide modified carbon ionic liquid electrode (CILE) has been investigated. Enzyme free electro-oxidation of glucose have greatly been enhanced at nanoscale $Ni(OH)_2$ as a result of electrocatalytic effect of Ni^{+2}/Ni^{+3} redox couple. The sensitivity to glucose was evaluated as 202 $\mu A\,mM^{-1}\,cm^{-2}$. From 50 μM to 23 mM of glucose can be selectively measured using platelet-like $Ni(OH)_2$ nanoscale modified CILE with a detection limit of 6 μM (S/N = 3). The nanoscale nickel hydroxide modified electrode is relatively insensitive to electroactive interfering species such as ascorbic acid (AA), and uric acid (UA) which are commonly found in blood samples. Long-term stability, high sensitivity and selectivity as well as good reproducibility and high resistivity towards electrode fouling resulted in an ideal inexpensive amperometric glucose biosensor applicable for complex matrices.

1. Introduction

Glucose sensing is greatly important in biotechnology, clinical diagnostics and food industry. Therefore, much effort has been made over the last several decades to develop electrochemical glucose sensors. Enzymatic glucose sensors based on the immobilization of glucose oxidase on various substrates are the topics of the most previous studies on this subject (Musameh et al., 2008; Jeykumari and Narayanan, 2008; Deng et al., 2008; Zhang et al., 2007; Lin et al., 2004). However, the greatest problem is naturally insufficient stability and loss of enzyme activity (Wilson and Turner, 1992) during immobilization process which affects sensitivity and reproducibility of glucose sensors. Another limitation is the severe interference caused by endogenous electroactive ascorbic acid (AA) and uric acid (UA) in blood samples since the electrode must be poised at +0.7 V (versus Ag/AgCl) or higher for electrochemical detection of hydrogen peroxide, a co-product of the enzymatic oxidation. Because of the mentioned drawbacks, developments of electrochemical non-enzymatic glucose biosensors have received continuous interest. The key issues for the applications in non-enzymatic glucose sensing include sensitivity, selectivity, and the prevention of fouling by adsorbed intermediates and some anions. The remedy for all of these issues lies in the properties of electrode materials because the electrocatalytic activity is the key factor that affects both the sensitivity and selectivity of glucose detection. Direct electro-oxidation of glucose on conventional carbon and noble metal electrodes (Li et al., 2007b; Sun et al., 2001; Salimi and Roushani, 2005; Matsumoto et al., 2003) was limited by the slow kinetics and surface fouling due to the adsorption of reaction intermediates in which repetitive pulsed potentials are required to remove adsorbed products. In order to overcome the low sensitivity, reproducibility and protection from electrode fouling, chemically modified electrodes (CMEs) have been designed. These CMEs can improve sensitivity and reproducibility but the most common problem in the use of CMEs is detachment of the catalyst from the substrate and the gradual decrease in electrochemical activity which limit their applications for long periods.

In recent years, the electrochemical sensors based on nanomaterials have been introduced. Fast growth in this field is due to their special physical and chemical properties such as increasing the surface area, mass transport and catalysis (Katz et al., 2004). Higher performance for glucose detection has been obtained using modified sensors and biosensors with metallic nanoparticles such as nanotubular array Pt (Yuan et al., 2005), mesoporous Pt (Park et al., 2003), Ni nanoparticles (You et al., 2003), Au nanoparticles (Jena and Raj, 2006; Kurniawan et al., 2006), Cu nanoparticles (Kang et al., 2007; Xu et al., 2006), Pt nanoparticles (Rong et al., 2007), Pt/Pb nanoparticles (Cui et al., 2007; Wang et al., 2008) and carbon nanotubes (Ye et al., 2004; Tan et al., 2008).

Enzymatic-free electro-oxidation of glucose is greatly enhanced at Ni and Cu compared to the other electrodes as a result of their

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electrocatalytic effect mediated by Ni^{+2}/Ni^{+3} or Cu^{+2}/Cu^{+3} redox couples (Luo et al., 1990; Luo and Kuwana, 1994; Casella et al., 1991). Many electrodes were modified by depositing Ni particles and nanoparticles on traditional electrode surfaces such as diamond (Ohnishi et al., 2002), gold (Casella and Gatta, 2000), carbon or graphite (You et al., 2003). Most of these applications originated from the application of the redox pair system of $Ni(OH)_2$/NiOOH, which is formed on the electrode surface in the alkaline medium. However, the serious problems with these modified electrodes are the gradual change in their catalytic activity and surface fouling as mentioned above.

In contrast to Cu and Ni nanomaterials which are unstable and easily oxidized in air and solution, hydroxide (or oxide) of these materials are relatively stable (Kang et al., 2007; Xu et al., 2006; Liu et al., 2006; Li et al., 2007a). Recently, there have been few attempts to construct glucose sensors based on the hydroxide (or oxide) of these nanomaterials (Zhuang et al., 2008; Cheng et al., 2008). For example, Zhuang et al., 2008, reported a new method for direct growth of CuO nanowires on Cu substrate for amperometric detection of glucose.

Recently, we proposed carbon ionic liquid electrode (CILE) as a high performance electrode with many good features and provision of high rates of electron transfer (Maleki et al., 2006; Safavi et al., 2006; Safavi et al., 2007a,b; Maleki et al., 2007). However, this electrode is not active towards glucose oxidation.

In our previous studies we introduced a simple method for fabrication of arrays of palladium nanoparticles on the CILE and demonstrated its electrocatalytic behaviour towards oxygen reduction, hydrogen peroxide and hydrazine oxidation (Safavi et al., 2007c; Maleki et al., 2008). In these studies, palladium nanoparticles have been deposited on the CILE surface by electrodeposition method. However, the general drawback with electrodeposited nanostructures is their relatively low stability, especially when they are used in hydrodynamic methods where detachment of nanoparticles is most probable.

In this work we report the fabrication of a novel non-enzymatic composite electrode based on mixing powdered nanoscale nickel hydroxide with graphite powder and ionic liquid (octylpyridinum hexafluorophosphate, $OPy^+PF_6^-$). In this way, an extraordinary stable nanosensor could be fabricated for highly sensitive amperometric detection of glucose. The electrode surface could be easily and reproducibly renewed by slight polishing on a smooth paper.

The mentioned composite electrode can be used directly as a non-enzymatic glucose biosensor. Due to its excellent resistance to surface fouling, long-term stability, renewable surface, high sensitivity and selectivity it could be suggested as an ideal glucose biosensor for application in different complex matrices.

2. Experimental

2.1. Reagents

1-Idooctane, pyridine, D-(+)-glucose were obtained from Merck. Ammonium hexafluorophosphate and graphite powder (mesh size <100 μm) were supplied by Fluka. A 0.01 mol l^{-1} glucose stock solution was prepared and stored in a refrigerator. $Ni(NO_3)_2{\cdot}6H_2O$, ammonia solution, sodium hydroxide and the other reagents were analytical grade from Merck. Deionized distilled water was used to prepare all solutions and rinse the electrodes.

The ionic liquid, octylpyridinium iodide was synthesized as described elsewhere (Fisicaro et al., 1996). $OPy^+PF_6^-$ was obtained by anion exchange of octylpyridinium iodide with ammonium hexafluorophosphate.

2.2. Synthesis of nanoscale $Ni(OH)_2$

Nanoscale $Ni(OH)_2$ was synthesized using a simple coordination precipitation procedure as previously reported (Xiao-yan and Jian-cheng, 2007) except that Tween-80 was replaced by Tween-100. Briefly, by adding concentrated ammonia (28 wt.%) to nickel nitrate solution (1 M), a deep blue coloured nickel hexammine complex solution was formed and added into a given amount of distilled water (with or without Tween-100 as a surfactant), the reaction was carried out under magnetic stirring for 1 h at 70 °C. Finally, a light green precipitate was separated and rinsed with distilled water and ethanol three times, respectively, to remove the adsorbed ions. The precipitate was then dried in a vacuum oven at 80 °C for 12 h. The final product was a green powder. Products obtained without surfactant in the reaction process were platelet-like shape and with the surfactant, Tween-100, were nanoneedle shape.

2.3. Electrode preparation

Nanoscale $Ni(OH)_2$ carbon ionic liquid electrode was prepared by hand-mixing of the weighed amounts of graphite powder, ionic liquid and $Ni(OH)_2$ nanoscale (60%:39%:1% w/w). A portion of the resulting paste was packed firmly into the cavity (1.8-mm i.d.) of a Teflon holder. The electric contact was established via a stainless steel handle. A new surface was obtained by smoothing the electrode onto a smooth paper. The nano $Ni(OH)_2$ composite carbon paste electrode (CPE) was constructed in the same way as nano $Ni(OH)_2$ composite CILE, except that ionic liquid was replaced by Nujol.

2.4. Apparatus

Voltammetric and amperometric measurements were performed using an Autolab electrochemical system (Eco-Chemie, Utrecht, The Netherlands) equipped with μAutolab type II and GPES software (Eco-Chemie). The electrochemical cell was assembled with a conventional three-electrode system: an Ag/AgCl/KCl (3 M) reference electrode (Metrohm) and a platinum disk as a counter electrode. Different working electrodes used in this study were a $Ni(OH)_2$ nanoscale carbon ionic liquid composite electrode (1.8-mm diameter) and a $Ni(OH)_2$ nanoscale carbon paste electrode (1.8-mm diameter). The cell was a one-compartment cell with an internal volume of 10 ml. All experiments were typically conducted at room temperature.

A model CM10 transmission electron microscope (TEM; Philips) was used to characterize the morphology and size of the nanoscale nickel hydroxide.

3. Results and discussion

TEM images of the nanoscale nickel hydroxide synthesized through coordination precipitation method shows a platelet-like nanostructure with a dimension in the range of 17–25 nm (Fig. 1a). As it is obvious, size-homogeneity of these particles is very well. By addition of a suitable amount of Tween-100 (below critical micelle concentration) as a surfactant during production process, the morphology of the product turned to the nanoneedles (Xiao-yan and Jian-cheng, 2007) with a length of 100–120 nm and an average diameter of about 50 nm (Fig. 1b). The discrepancy between the morphologies obtained from TEM of different samples may be related to the soft template effect of the surfactant as has been described previously (Xiao-yan and Jian-cheng, 2007).

Fig. 2A shows the cyclic voltammogram of the modified electrode in 0.5 M NaOH solution. The anodic and cathodic peaks in 0.5 M NaOH alkaline solution are assigned to the Ni^{+2}/Ni^{+3}

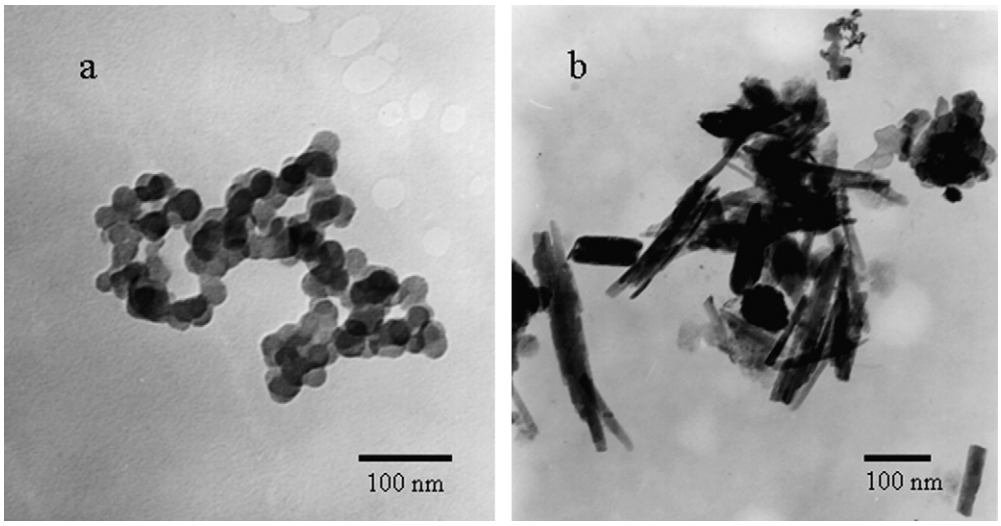

Fig. 1. TEM images of nanoscale nickel hydroxide products in the absence (a) and presence (b) of Tween-100 as surfactant.

redox couple. The peak currents increased gradually during successive scans until a steady state was reached. In alkaline solutions nanoscale $Ni(OH)_2$ was oxidized to NiOOH and turned to $Ni(OH)_2$ by potential cycling (Luo et al., 1990). When the background current became stable, a solution of glucose was injected into the electrolytic cell, and its response was measured.

The CILE itself (without nanoscale $Ni(OH)_2$) is not active toward glucose oxidation (curve a in Fig. 2B).

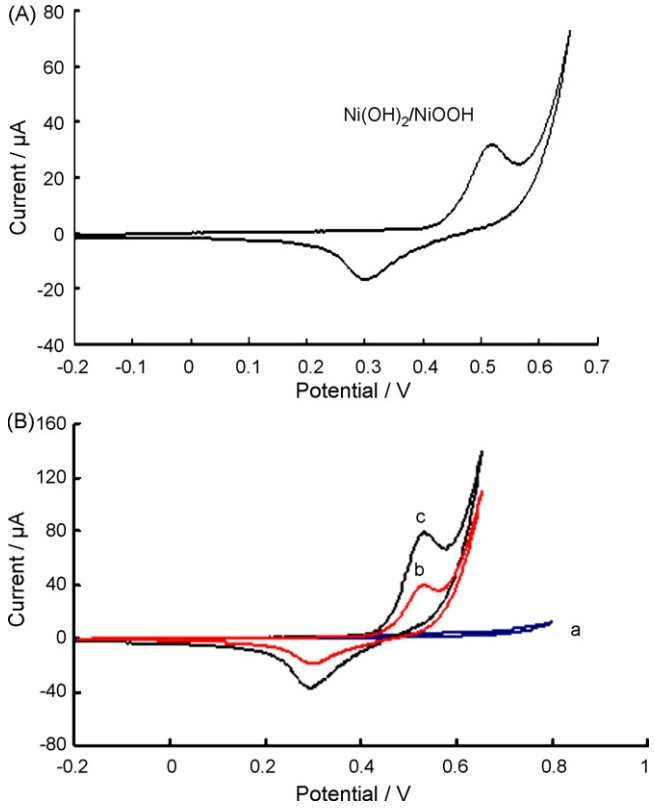

Fig. 2. (A) Cyclic voltammograms obtained in 0.5 M NaOH solution at nanoscale (platelet-like) modified CILE after 20 repetitive scans, (B) cyclic voltammograms obtained for 1 mM glucose in 0.5 M NaOH solution at (a) CILE, (b) $Ni(OH)_2$ nano platelet-like modified CILE in the absence of glucose and (c) $Ni(OH)_2$ nano platelet-like modified CILE in the presence of 1 mM glucose.

The electocatalytic activity of the modified electrode towards oxidation of glucose in an alkaline solution is shown in Fig. 2B. This is attributed to the well-known catalytic effect of the Ni^{+2}/Ni^{+3} redox couple for oxidation of glucose to glucolactone according to the following reactions (Zhao et al., 2007):

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

$$NiO(OH) + \text{glucose} \rightarrow Ni(OH)_2 + \text{glucolacton}$$

In the present work, the Ni^{+2}/Ni^{+3} species on the electrode surface acts as a catalyst for the oxidation of glucose. When glucose diffuses to the electrode surface, it is rapidly oxidized to glucolactone by the Ni^{+3} species on the electrode. This electrochemical behaviour is different from typical mediated catalytic oxidation in which the cathodic peak current is expected to decrease. An increase in the anodic peak current and the cathodic peak current after glucose addition is believed to be due to the fact that the Ni^{+2}/Ni^{+3} redox couple serves a double function of the electronic medium and catalyst, synchronously (Zhao et al., 2007).

In order to study the anti fouling behaviour of the electrode, repetitive cyclic scans were performed in a solution of glucose (1 mM), and the responses were measured. It was observed that during repetitive cycles, the peak potential and the current due to the oxidation of glucose did not change. This suggests that the intermediates or reaction products were not deposited on the electrode surface and thus electrode fouling, a common and serious limitation for application of glucose sensor, did not take place here.

The effect of scan rate on peak current for oxidation of glucose (1 mM) showed a linear relationship between peak current and square roots of scan rate demonstrating a diffusion controlled electron transfer process.

In order to investigate how the shape and size of the $Ni(OH)_2$ nanoscale affects kinetics of electron transfer and sensitivity, the composite electrodes were prepared using two different kinds of synthesized nanoscale $Ni(OH)_2$ (platelet-like and nanoneedle shapes).

A significant difference was observed between both cyclic voltammograms and amperometric responses obtained using platelet-like $Ni(OH)_2$ nanoscale modified CILE and the nanoneedle $Ni(OH)_2$ composite electrodes (Fig. 3). As can be seen in TEM images (Fig. 1), two different morphologies of nanoscale $Ni(OH)_2$ have been formed depending on the conditions that have been employed during synthetic process of these nanostructures. Size,

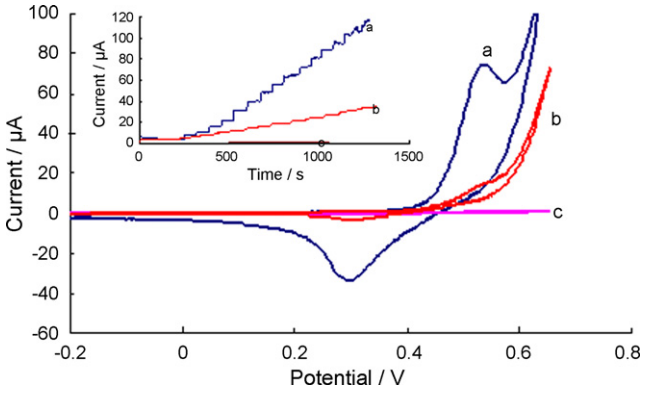

Fig. 3. Cyclic voltammograms obtained for 1 mM glucose in 0.5 M NaOH solution at (a) $Ni(OH)_2$ platelet-like modified CILE (b) nanoneedle $Ni(OH)_2$ modified CILE (c) $Ni(OH)_2$ platelet-like modified CPE. The inset displays steady-state current–time responses of glucose at +0.55 V subjected to various concentrations of glucose in 0.5 M NaOH at (a) $Ni(OH)_2$ platelet-like shape modified CILE (b) nanoneedle $Ni(OH)_2$ modified CILE (c) nanoscale $Ni(OH)_2$ modified CPE.

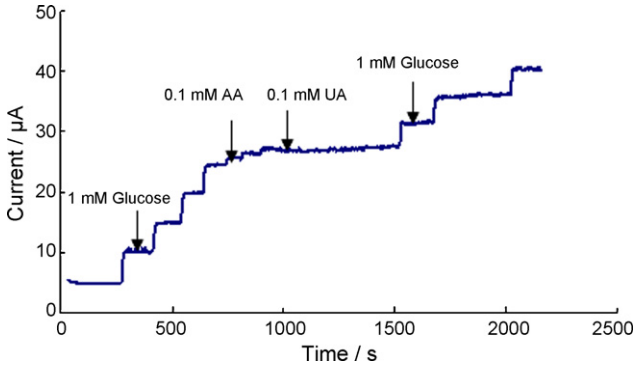

Fig. 4. Amperometric response of glucose (1 mM) in the absence and presence of 0.1 mM AA and UA, at nanoscale $Ni(OH)_2$ modified CILE in 0.5 M NaOH at an applied potential of +0.55 V.

shape and morphology of nanoscale materials significantly affect their catalytic behaviour (Safavi et al., 2008). Platelet-like $Ni(OH)_2$ nanoscale structure show smaller diameter, well size and shape homogeneity rather than nanoneedle $Ni(OH)_2$ structure. In order to construct two types of the composite electrodes the same percentage of the modifier (platelet-like $Ni(OH)_2$ nanoscale and nanoneedle $Ni(OH)_2$), 1% (wt.%), was used for each composite electrode. The results showed that the current signal at the $Ni(OH)_2$ platelet-like modified CILE was significantly higher than that with the nanoneedle $Ni(OH)_2$ modified CILE. For further clarification of these results, chronoamperometric signals towards glucose oxidation were obtained for both composite electrodes. The results showed a four fold increase in the active surface area of the $Ni(OH)_2$ platelet-like modified CILE compared to nanoneedle $Ni(OH)_2$ modified CILE. Considering the fact that the same weight percentage of both nanostructures (1%) were used for constructing the electrodes, it could be concluded that the higher sensitivity in the case of nano $Ni(OH)_2$ platelet-like modified CILE is mainly due to its higher active surface area compared to nanoneedle $Ni(OH)_2$ modified CILE, although the effect of shape and morphology of these nanostructures cannot be ruled out.

Table 1
Comparison of various non-enzymatic glucose sensor

Glucose sensor	Linear range	Surface fouling	Long-term storage stability	Sensitivity ($\mu A\,mM^{-1}\,cm^{-2}$)	Real sample	Reference
Copper nanocluster/multi-wall carbon nanotube (Cu–CNTs–GCE)	0.7–3.5 mM	No	35 days	251.38	Blood serum	Kang et al. (2007)
Functionalized Cu nanoparticles	1 μM–5 mM	Decreased fouling	60 days	*	Blood serum	Xu et al. (2006)
Pt-nanotube arrays electrode	2–14 mM	Yes	*	*	*	Yuan et al. (2005)
Au nanoparticle modified transducer electrode	0–8 mM	No	One week	179	*	Jena and Raj (2006)
Ni powder modified electrode	0.5–5000 μM	No	*	40	Blood serum	You et al. (2003)
Ni nanoparticle modified carbon paste electrode	1.0 μM–1.0 mM	*	One week	*	Honey	Cheng et al. (2008)
Porous Au electrode	2–10 mM	Yes	48 h	11.8	*	Li et al. (2007b)
Multi-walled carbon nanotube modified electrode	2 μM–11 mM	*	*	4.36	*	Ye et al. (2004)
Copper-based nanoparticles supported on the gold surface	0.1 μM–5 mM	No	Two months	*	*	Liu et al. (2006)
Nickel electrode	0.1–2.5 mM	No	*	*	Blood serum	Zhao et al. (2007)
PtPbNP/MWCNT	Up to 11 mM	*	*	17.8	*	Cui et al. (2007)
Pt nanoparticles supported on carbon nanotubes	1–26.5 mM	Yes	*	*	*	Rong et al. (2007)
Mesoporous Pt electrode	0–10 mM	Yes	*	9.6	*	Park et al. (2003)
CuO nanowire modified electrode	0.4 μM–2 mM	No	50 days	2450	Blood serum	Zhuang et al. (2008)
Multiple-branching carbon nanotube forest	1–11 mM	*	*	60	*	Tan et al. (2008)
Nanoporous Pt–Pb networks	1–16 mM	Yes	*	*	*	Wang et al. (2008)
Present work	0.05–23 mM	No	100 days	202	Blood serum	–

* Not reported.

Table 2
Determination of glucose in blood serum samples

Sample*	Added (mM)	Enzymatic method reported in a local hospital (mM)	Proposed non-enzymatic method (mM)	Recovery (%)
1	–	8.1	7.70 ± 0.09	–
	0.1	–	7.80 ± 0.11	100
	0.2	–	7.90 ± 0.08	100
	0.4	–	8.10 ± 0.13	100
2	–	3.7	3.20 ± 0.12	–
	0.1	–	3.29 ± 0.15	90
	0.2	–	3.39 ± 0.09	95
	0.3	–	3.50 ± 0.09	100

* Triplicate analysis was performed for each sample.

In order to elucidate the role of ionic liquid as the binder in this new composite electrode, its electrocatalytic effect on glucose oxidation was compared with an electrode made with the same nano $Ni(OH)_2$ but using Nujol as the binder instead of ionic liquid. The results in Fig. 3 show the obvious superiority of the presence of ionic liquid in the composite electrode. In fact the nanoparticle microenvironment is known to be greatly influenced by the support on which it is deposited. The advantages of the presence of ionic liquid in carbon paste electrode have been discussed in our previous reports (Maleki et al., 2007).

The ratio of nanosized $Ni(OH)_2$ to the graphite and ionic liquid did not have a significant effect on the electrochemical activity towards glucose, but an increasing amount of $Ni(OH)_2$ caused the background current to increase sharply (not shown). The presence of 1% $Ni(OH)_2$ nano platelet in the electrode material is sufficient to give the optimum signal to noise ratio for glucose.

As the inset of Fig. 3 shows, very well defined amperometric current responses were obtained at the proposed glucose sensor in 0.5 M NaOH at a potential of +0.55 V. Oxidation reaction is very fast and the current reaches to a steady-state level within 5–7 s upon successive additions of glucose.

The sensor displays two linear ranges from 50 μM to 1 mM and 0.5–23 mM with correlation coefficients of 0.9987 and 0.9974, respectively. The experimental limit of detection, based on a signal-to-noise ratio of 3, was 6 μM and the sensitivity of the sensor was 202 $\mu A\,mM^{-1}\,cm^{-2}$, using the calibration graph in the lower range. A Comparison between some efficient non-enzymatic glucose sensors are presented in Table 1. It can be seen that the proposed glucose sensor shows a good superiority in terms of sensitivity, selectivity, long-term stability, linear calibration range and resistance towards electrode fouling.

3.1. Interference study

Ascorbic acid and uric acid present in physiological fluids are the most important interferences for direct electrochemical oxidation of glucose on different electrodes especially non-enzymatic sensors (Yuan et al., 2005). The normal physiological level of glucose is about 3–8 mM, which is much higher than the concentrations of interfering species like UA (0.1 mM) and AA (0.1 mM). Therefore, in the present work, we studied the interference effect of 0.1 mM UA and 0.1 mM AA on the amperometric response of 1 mM glucose. Based on the above results, when applying a potential of +0.55 V to the $Ni(OH)_2$ nanoscale carbon ionic liquid composite electrode, the Ni^{+3} species is produced on the electrode surface which acts as a catalyst towards the oxidation of glucose generating Ni(II) species, and glucolactone, simultaneously. This electrocatalytic effect towards oxidation of glucose is responsible for good selectivity observed on the proposed sensor in the presence of the most important interferences for direct electrochemical oxidation of glucose (Fig. 4).

3.2. Stability and reproducibility

The proposed sensor was stored in air at ambient conditions and its sensitivity was checked every week. The response of the sensor was 95% of its initial value after 100 days which shows long-term stability and very good sensitivity for the analysis of real samples.

Six successive amperometric measurements of 2 mM glucose on one modified electrode yielded a reproducible current with the relative standard deviation (R.S.D.) of 3.4%, demonstrating that the electrode was not poisoned by the oxidation product and can be used repeatedly for the detection of glucose. In addition, three electrodes were made and the responses of the electrodes were measured towards 2 mM glucose. In this case, the R.S.D. was obtained as 4.1% confirming that the fabrication method was highly reproducible.

3.3. Real sample analysis

To evaluate the ability of the sensor for routine analysis, the sensor was applied to the determination of glucose in blood serum samples. Here, 50 μl of blood serum sample was added to 10 ml of 0.5 M NaOH and the amperometric response of glucose was recorded at +0.55 V. The results are presented in Table 2 ($n = 3$). This table also shows that there is a very good agreement between the results obtained by the proposed sensor and those obtained by application of a routine enzymatic method (using glucose oxidase) in a local hospital.

4. Conclusion

Fabrication of a highly sensitive and selective enzymatic-free glucose biosensor nanocomposite electrode has been explained using $Ni(OH)_2$ nanoscale material. The presence of ionic liquid as a binder increased the sensitivity of the sensor and is believed to be responsible for the high resistance towards electrode fouling (Maleki et al., 2007). High stability, sensitivity, selectivity and reproducibility as well as very fast response time, ease of preparation, low cost and surface renewal made this sensor ideal for detection of glucose in real samples such as blood serum samples.

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