



In situ synthesis of Ni(OH)₂/TiO₂ composite film on NiTi alloy for non-enzymatic glucose sensing



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ABSTRACT

A one-step potential cycling technique for *in situ* synthesis of electroactive Ni(OH)₂ and protective TiO₂ composite film on NiTi alloy is described. The Ni(OH)₂/TiO₂ composite film can be used directly as the electrode in a non-enzymatic glucose sensor. This binder-free sensor boasts a high glucose sensitivity of 192 μA mM⁻¹ cm⁻², short response time of less than 1 s, and detection limit of 8 μM. In addition, the stable and protective TiO₂ extends the linear range to 14 mM and provides excellent long-term stability. This novel fabrication method not only simplifies the preparation of high-performance non-enzymatic glucose sensing materials, but also can be readily extended to the fabrication of other transition metal-based biosensors.

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1. Introduction

Development of efficient, reliable, and cost-effective biosensors for accurate and convenient detection of glucose is highly desirable in the food industry, biotechnology, and clinical diagnosis. In particular, accurate monitoring of the glucose concentration in biological fluids is crucial as diabetic mellitus has become the second major public health problem affecting hundreds of millions of people worldwide [1,2]. Currently, most of the commercial glucose meters are based on the working principle of immobilization of enzymes such as glucose oxidase (GOx) and glucose dehydrogenase (GDH) [3]. Despite the high sensitivity and excellent selectivity, enzyme-immobilized electrodes suffer from intrinsic drawbacks such as poor reproducibility, thermal and chemical instability, and high cost [4]. To overcome these drawbacks, efforts have been made to fabricate enzyme-free glucose sensors based on electroactive materials with catalytic abilities that can oxidize glucose directly on the electrode surface [5,6]. Various types of metals and alloys (e.g. Pt, Au, Pt-Pb, Ni, Cu, Ni-Ti, Ni-Cu) [7–13] and transition metal oxides and hydroxides (e.g. Co₃O₄, NiO, Ni(OH)₂, Cu(OH)₂) [14–19] have been explored. Among them, Ni-based materials have attracted

special attention due to the low cost and high electrocatalytic activity in glucose oxidation [20–22].

Since Fleischmann et al. [23] elucidated the mechanism of glucose oxidation on Ni involving the Ni²⁺/Ni³⁺ redox couple in an alkaline medium, various forms of nickel oxides as well as hydroxides have been adopted in glucose sensing probes [21,24–28], for instance, hollow microspheres, nanoparticles, nanoflakes, nanowires, and nanosheets. They have also been integrated with carbon-based nanomaterials such as carbon nanotubes (CNT) and graphenes to form hybrids [29–31] to improve glucose detection. However, fabrication of glucose sensors using these materials involves immobilization on a conventional electrode [24,28], such as glassy carbon electrode (GCE). Not only is the preparation process tedious and time consuming, but also adhesion between the active materials and underlying electrode tends to be weak. Although some improvements have been made by using polymer binders such as Nafion [25], they are inert in glucose sensing and produce high contact resistance consequently compromising the sensor performance.

These aforementioned drawbacks can be overcome by *in situ* synthesis of the electroactive materials on the working electrode. Near-equiatomic nickel-titanium alloy, also known as nitinol, is a common and widely used biomedical material due to its unique properties, such as the shape memory effect and superelasticity [32]. In this paper, a simple one-step and low-cost technique to fabricate a non-enzymatic glucose sensor on NiTi alloy is described. After potential cycling in a concentrated alkaline solution, a

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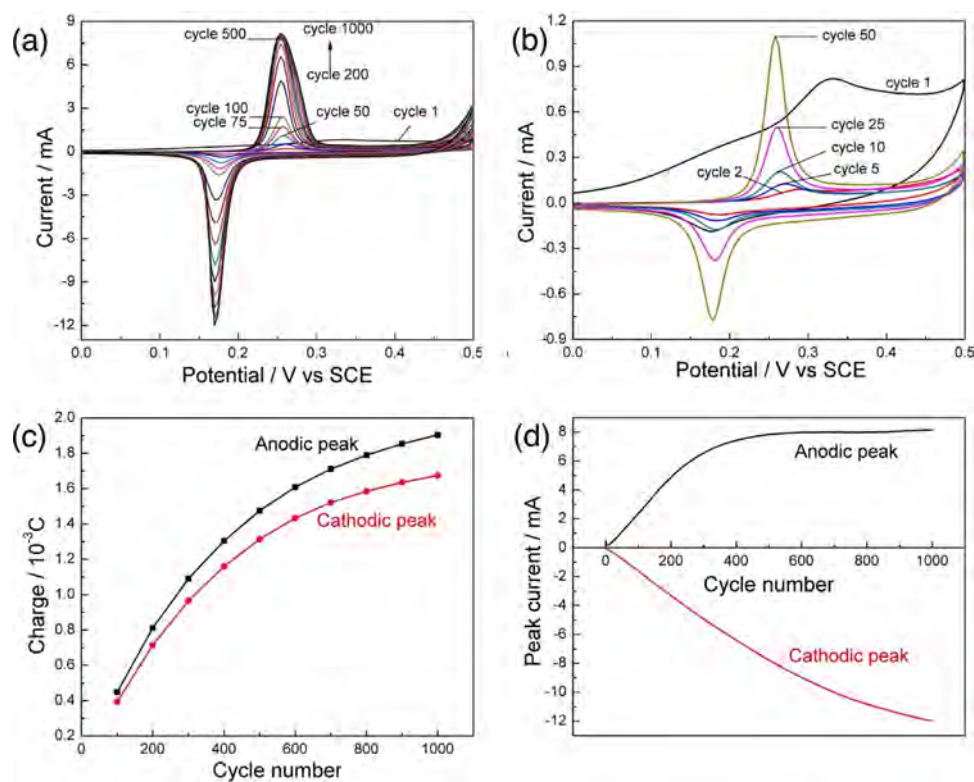


Fig 1. (a) Series of cyclic voltammograms (CV) acquired from the NiTi alloy at a scanning rate of 200 mV/s for 1000 cycles in 6 M NaOH. (b) First 50 cycles shown in (a). (c) Plots of charges integrated from anodic and cathodic peaks in CV versus number of cycles. (d) Plots of peak currents in CV versus number of cycles. The peak currents are derived from the anodic and cathodic peaks centered at 0.26 V and 0.18 V, respectively.

composite film consisting electroactive Ni(OH)₂ and protective TiO₂ produced on the NiTi alloy can be adopted directly as a glucose sensor without binders or tedious post-treatments. Compared to the Ni(OH)₂ electrode fabricated on pure Ni using the same procedures, the Ni(OH)₂/TiO₂ electrode has a wider linear range in addition to ultrafast response and excellent long-term stability.

2. Experimental details

NiTi alloy (50.8 at.% Ni) sheets were acquired from Nitinol Devices & Components Co. (NDC, USA) and chemical reagents including sodium hydroxide (NaOH), D-(+)-Glucose, L-ascorbic acid (AA), and uric acid (UA) were purchased from International Laboratory (IL, USA) and used as received. All the aqueous solutions were prepared with doubly distilled water. Unless otherwise specified, the electrochemical experiments were performed in 0.1 M NaOH electrolyte after the solutions were purged with nitrogen for approximately 20 min. The glucose stock solutions were kept overnight before use and stored at 4 °C.

The electrochemical experiments were performed on a CHI 600C workstation (CH Instruments, China) with the conventional three-electrode configuration. A Pt foil (1 × 1 cm²) and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The electrochemical experiments were performed at room temperature (22 ± 2 °C) and the reported potentials were referenced against SCE.

The NiTi alloy sheets were cut into small pieces with dimensions of 1 × 1 × 0.15 cm³, polished to a mirror finish, and ultrasonically cleaned in acetone, ethanol, and deionized water successively. In a typical synthesis, the Ni(OH)₂/TiO₂ composite film was prepared by potential cycling of the NiTi alloy (exposed area of 1 × 1 cm²) between 0 and 500 mV at a scanning rate of 200 mV/s for 500 cycles in 6 M NaOH (denoted as Ni(OH)₂/TiO₂ electrode). In addition, pure

Ni foils (purity ≥ 99.99%) were treated by the same procedures to serve as the control (denoted as Ni(OH)₂ electrode).

Cyclic voltammetry was carried out in the quiescent solution and amperometric measurements were performed under continuous stirring. Electrochemical impedance spectroscopy (EIS) was performed on the Zennium electrochemical workstation (ZAHNER, Germany) with the same three-electrode configuration in an electrolyte solution of 0.1 M NaOH containing 5 mM glucose and a frequency range from 0.1 Hz to 1 MHz with an AC probe amplitude of 5 mV.

Field-emission scanning electron microscopy (FE-SEM, JSM-7001F, JEOL) was performed to observe the surface morphology of the samples and elemental depth profiles were acquired by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo). The argon sputtering rate was 0.3 nm/s and the binding energies were referenced to the C 1s peak (285 eV).

3. Results and discussion

3.1. Fabrication of Ni(OH)₂/TiO₂ electrode

The Ni(OH)₂/TiO₂ electrode is fabricated by potential cycling of the NiTi alloy in a concentrated alkaline medium. Fig. 1(a) shows the overlay of the consecutive cyclic voltammograms (CV) acquired at a scanning rate of 200 mV/s for 1000 cycles in 6 M NaOH. The characteristic anodic and cathodic peaks at about 0.26 V and 0.18 V, respectively, can be attributed to the redox couple of Ni²⁺/Ni³⁺ according to the following reaction [23]:

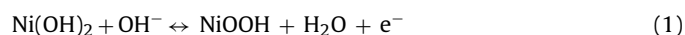


Fig. 1(b) presents the first 50 cycles in Fig. 1(a). The enhanced baseline in the first sweep is ascribed to irreversible oxidation of

metallic Ni to Ni(OH)₂ in the alkaline solution at a positive potential according to the following reaction [21]:



The marked difference in the background current between NiTi (Fig. 1(b)) and pure Ni (Fig. S1(b)) in the first sweep indicates irreversible anodization of Ti to be titanium oxide on the NiTi alloy [33]. It is verified by XPS and will be discussed later. Since oxidation of Ni and Ti is irreversible, a larger oxidation current is only observed in the first trace and vanishes in the reverse and subsequent ones.

Fig. 1(c) shows the dependence of the anodic and cathodic charges integrated from the CVs on the number of voltammetric cycles. It can be inferred that the transferred charges are proportional to the amount of nickel hydroxide generated by oxidation of the Ni-based substrate. The gradual increase in the charges transferred during the anodic and cathodic processes indicates that the electroactive species Ni²⁺/Ni³⁺ accumulate progressively on or near the surface following Reaction (2) and these species have good electrochemical reversibility according to Reaction (1). Potential cycling in the alkaline solution in the Ni²⁺/Ni³⁺ redox range is often utilized to “activate” Ni or its oxide into electroactive species for glucose sensing [24,34–36]. However, the concentration of the alkaline solution in previous studies such as 0.1 M or 1 M is too diluted to make full use of the surface Ni.

Although the transferred charges continue to rise as shown in Fig. 1(d), the anodic peak current no longer increases after 500 cycles and stabilizes thereafter at 8 mA. As the anodic peak current depends on the amount of electroactive species Ni²⁺/Ni³⁺ and kinetics of Reaction (1), stabilization after 500 cycles indicates that the optimal thickness of the surface activated film in which electrons and protons can transfer or exchange effectively is achieved [37–39]. Further cycling draws more underlying Ni and thickens the surface layer. While the species on the outer active surface are freely accessible, the redox behavior of the inner active species begin to exhibit hysteresis as reflected by the broadening of anodic peak in Fig. 1(a). Therefore, the best glucose sensing performance is expected after potential cycling for 500 cycles and the process is adopted in subsequent experiments.

3.2. Surface characterization

The surface morphologies of the pristine NiTi alloy, as-prepared Ni(OH)₂/TiO₂, and Ni(OH)₂ electrodes examined by SEM are shown in Fig. S2. The low-magnification images reveal that these three surfaces are nearly the same and show scratches resulting from polishing. According to the high-magnification images, few morphological features or differences can be observed from the pristine NiTi and Ni(OH)₂/TiO₂ electrode, indicating that no morphological changes occur during potential cycling. With regard to the pure Ni, after cycling, a rough surface with wrinkles is observed and it is a characteristic feature of the modified Ni(OH)₂ surface [40–42].

Fig. S3 shows the elemental depth profiles of the films prepared by cycling NiTi and pure Ni in 6 M NaOH for 500 cycles. The distribution of O provides information about the thickness of surface activated films. Based on a sputtering rate of 0.3 nm/s, the film thickness estimated by the location at which oxygen concentration drops below 30% is 15 and 9 nm for Ni(OH)₂/TiO₂ and Ni(OH)₂, respectively. The Ni/Ti ratio is nearly constant indicating that there is no segregation during potential cycling.

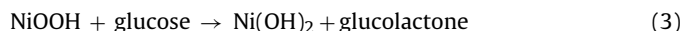
The evolution of the Ni 2p, Ti 2p, and O 1s spectra of Ni(OH)₂/TiO₂ electrode with sputtering time is shown in Fig. 2(a–c). On the electrode surface (0 s), Ni and Ti mainly exist in the form of Ni(OH)₂ and TiO₂, respectively. After sputtering for 10 s, peaks of metallic Ni at 853.0 and 870.2 eV begin to appear, while Ti is still in form of TiO₂ with the Ti 2p_{3/2} peak at 459.1 eV. After sputtering for 50 s, metallic Ni becomes dominant and the broad Ti peak can

be deconvoluted into six peaks as shown in Fig. 2(e), indicating the presence of Ti suboxides such as Ti³⁺ and Ti²⁺ (corresponding to Ti₂O₃ and TiO). Further sputtering removes all hydroxides/oxides and exposes the metallic substrate. As for the Ni(OH)₂ electrode, the Ni 2p, and O 1s spectra acquired at different sputtering time are shown in Fig. S4. The Ni 2p spectra disclose an evolution trend similar to that of Ni(OH)₂/TiO₂. At the surface Ni is primarily in the form of Ni(OH)₂ and gradually becomes metallic Ni with the increase of sputtering time. The O 1s spectra show two clear peaks corresponding to the binding states of hydroxide and oxide, indicating the existence of NiO at the hydroxide-metal interface. Based on above analysis, the qualitative composition of the surface activated films is presented in Fig. 3. After cycling in the concentrated alkaline solution, a Ni(OH)₂ layer is expected to form on the Ni-based electrode. Owing to the higher affinity of Ti to oxygen, the presence of Ti in the NiTi alloy results in coexistence of stable and protective titanium oxide with and underneath the top Ni(OH)₂ layer.

3.3. Electrocatalytic oxidation of glucose

Fig. 3(c) shows the CVs of the pristine NiTi alloy, as-prepared Ni(OH)₂/TiO₂, and Ni(OH)₂ electrodes in the range of 0.2–0.6 V at a scanning rate of 50 mV/s. While there is no obvious peak from the pristine NiTi alloy, a pair of well-defined peaks corresponding to the Ni²⁺/Ni³⁺ redox couple prior to the onset of oxygen evolution can be observed for the other two electrodes. As expected, because there are more active sites on Ni(OH)₂ electrode, its redox peaks area is larger than that of Ni(OH)₂/TiO₂ electrode.

The electrocatalytic properties of the Ni(OH)₂/TiO₂ electrode towards glucose are investigated by CV at different scanning rates with addition of 5 mM glucose. As shown in Fig. 4(a), both the anodic and cathodic peak currents exhibit a linear relationship with the square root of the scanning rates indicating a typical diffusion-controlled electrochemical process, which is sensitive to the glucose concentration and desirable in quantitative analysis [43]. Fig. 4(b) shows the CVs of the Ni(OH)₂/TiO₂ electrode in the absence and presence of glucose at different concentrations. Increase of the glucose concentration from 0 to 10 mM leads to the corresponding larger anodic peak current and smaller cathodic peak current, demonstrating the good catalytic effect of the Ni²⁺/Ni³⁺ redox couple in glucose oxidation [23]. When glucose diffuses to the electrode surface, it is rapidly oxidized by Ni³⁺ according to the following irreversible reaction [26]:



Ni³⁺ is reduced to Ni²⁺ and oxidized back to Ni³⁺ again at the anodic potential according to Reaction (1). As aforementioned, this electrochemical reaction is a diffusion-controlled process. A larger concentration of glucose in the solution results in more glucose molecules diffusing to the electrode surface and be involved in the catalytic reaction, consequently increasing the anodic peak current and decreasing the cathodic peak current.

3.4. Amperometric detection of glucose

The potential applied in amperometry is optimized by chronoamperometry performed at different potentials with successive addition of 1 mM glucose. As shown in Fig. 4(c), the maximum current response to each addition of glucose is observed at 0.5 V, while the oxygen evolution reaction (OER) occurs at a higher potential, leading to the elevated current background and lower current response. The effects of the applied potential on the electron transfer resistance is studied by EIS (Fig. 4(d)). The diameters of the semicircle at higher frequencies decrease with increasing potentials, indicating that higher potentials facilitate the electron transfer reaction. However, when the potential is increased to 0.55 and

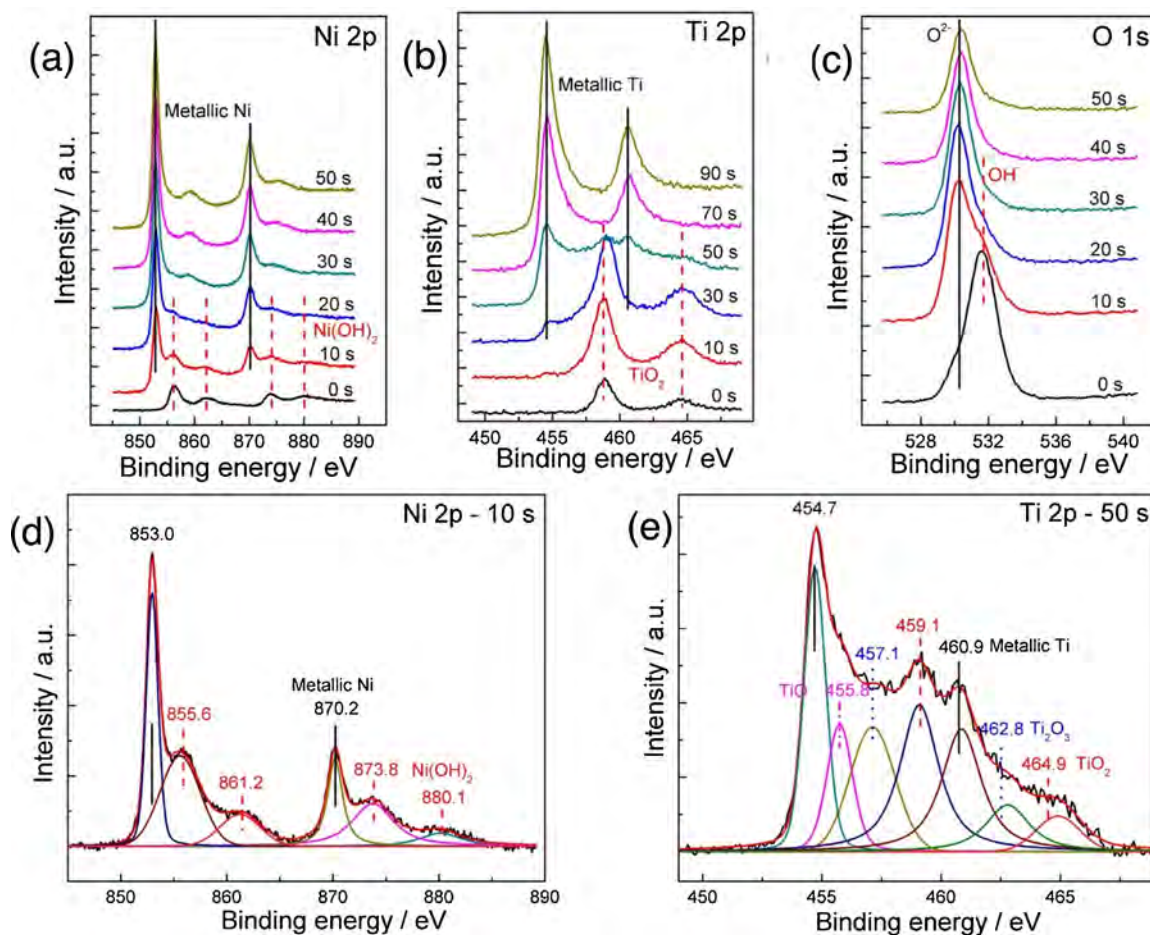


Fig. 2. High-resolution XPS spectra of the Ni(OH)₂/TiO₂ electrode at different sputtering time: (a) Ni 2p, (b) Ti 2p, and (c) O 1s. Deconvoluted XPS spectra: (d) Ni 2p after sputtering for 10 s and (e) Ti 2p after sputtering for 50 s.

0.6 V, the electron transfer resistance drops sharply. As the electroactive Ni(OH)₂ on the surface of Ni(OH)₂/TiO₂ electrode can serve as catalyst for water oxidation in alkaline media [44], OER occurs at an onset potential of ~0.525 V according to Fig. 3(c). Thus the drop of electron transfer resistance can be ascribed to oxidation of water on the electrode surface at these high potentials instead of the catalytic reaction between Ni²⁺/Ni³⁺ species and glucose. Therefore, 0.5 V is the optimal potential for glucose determination.

The glucose sensing performance of the Ni(OH)₂/TiO₂ electrode was investigated by chronoamperometry. Fig. 5(a) shows the amperometric response of the Ni(OH)₂/TiO₂ electrode towards successive addition of glucose at an applied potential of 0.5 V under stirring. The Ni(OH)₂/TiO₂ electrode produces a sensitive current response towards glucose at a concentration as low as 1 μM (Fig. 5(a), left inset). Moreover, it responds nearly instantaneously after addition of 1 mM glucose and reaches a steady state within 1 s (Fig. 5(a), right inset), indicating ultrafast and sensitive detection of glucose. The corresponding calibration curve (Fig. 5(b)) exhibits a linear range from 0.03 mM to 14 mM with a sensitivity of 192 μA mM⁻¹ cm⁻² (correction coefficient *R* = 0.998). The limit of detection (LOD) is found to be 8 μM at a signal-to-noise (S/N) ratio of 3. Fig. S7 shows the amperometric response of Ni(OH)₂ electrode under the same conditions. The corresponding calibrated linear range, sensitivity, and LOD are 0–8 mM, 319 μA mM⁻¹ cm⁻² (correction coefficient *R* = 0.995), and 14 μM, respectively. Although the sensitivity is lower due to less electroactive sites on its surface, the Ni(OH)₂/TiO₂ electrode exhibits a wider linear range than

the Ni(OH)₂ electrode possibly because of the presence of TiO₂. The limited linear range of glucose sensing is generally due to the saturated catalytic reaction kinetics and saturated diffusion of analytes [43]. For example, additional diffusion barrier membranes are used to produce diffusion delay of glucose to extend the linear range of enzymatic biosensors [45–47]. However, an obvious compromise for such extension is the decreased sensor sensitivity and longer detection time [45]. As discussed before, oxidation of glucose on Ni(OH)₂/TiO₂ is diffusion-controlled and so diffusion of glucose plays a critical role in the linear range of the sensor. The electrochemically inert TiO₂ separates the electroactive sites and covers a portion of the electrode surface, thereby reducing the effective flux of glucose diffusing to the electroactive sites and increasing the linear range. In general, the sensitivity of the Ni(OH)₂/TiO₂ electrode is not reduced substantially due to the presence of TiO₂ (192 μA mM⁻¹ cm⁻² versus 319 μA mM⁻¹ cm⁻²), but the linear range is greatly widened (14 mM versus 8 mM) while an ultrafast response time is retained (within 1 s).

The key performance parameters of previously reported Ni-based non-enzymatic glucose sensors were compared with those of our Ni(OH)₂/TiO₂ sensor in Table 1. Clearly, shorter response time and wider linear range are attractive features of the Ni(OH)₂/TiO₂ sensor. The good performance can be attributed to the presence of TiO₂, excellent electrocatalytic properties of the activated Ni²⁺/Ni³⁺ species as well as fast electron transfer between the *in situ* synthesized surface Ni(OH)₂/TiO₂ layer and underlying metallic current collector.

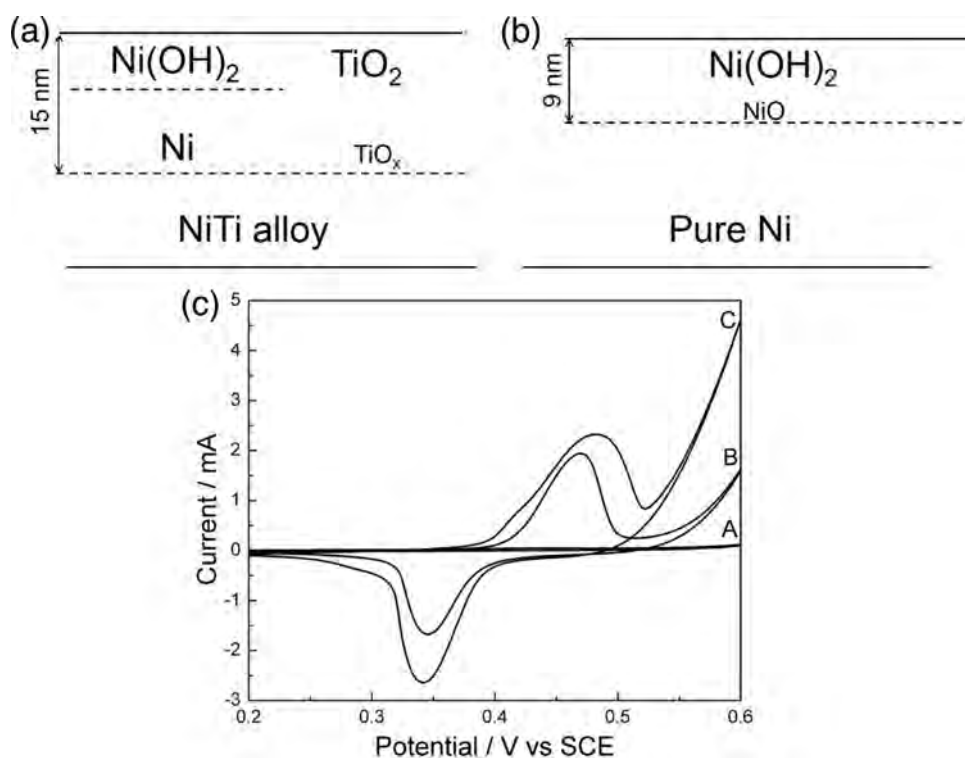


Fig. 3. Schematic illustration of the surface films formed on (a) NiTi alloy and (b) Ni after potential cycling in 6 M NaOH for 500 cycles. (c) Cyclic voltammograms of (A) Polished NiTi alloy, (B) Ni(OH)₂/TiO₂ electrode, and (C) Ni(OH)₂ electrode in 0.1 M NaOH at a scanning rate of 50 mV/s.

3.5. Interference study, reproducibility and detection of glucose in serum samples

Selectivity is of great importance in glucose sensing as other biomolecules like ascorbic acid (AA), and uric acid (UA) that co-exist with glucose in blood can be oxidized simultaneously at the applied potential, thus interfering the detection of glucose. Considering that the physiological concentration of glucose is much higher than those of the interfering species, selectivity of Ni(OH)₂/TiO₂ and Ni(OH)₂ electrodes is evaluated by measuring their amperometric response towards successive addition of 5 mM glucose, 0.1 mM AA, 0.1 mM dopamine (DA), 0.1 mM sucrose, and 0.1 mM UA at an

applied potential of 0.5 V. As shown in Fig. 5(c), a prominent current response is obtained after addition of glucose, whereas the other four interfering species only give rise to fairly small and negligible responses. These results indicate that the Ni(OH)₂/TiO₂ and Ni(OH)₂ electrodes possess sufficient selectivity for glucose sensing in real samples.

With regard to the reproducibility, six consecutive amperometric measurements of 5 mM glucose by a single Ni(OH)₂/TiO₂ electrode show a relative standard deviation (RSD) of 3.52%, implying that the electrode is not poisoned by the oxidized products and can be used repeatedly. The batch-to-batch reproducibility is evaluated by the current responses of six independently

Table 1
Comparison of results related to glucose detection using non-enzymatic Ni-based electrodes.

Electrode	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	Linear range (mM)	LOD (μM)	Response time (s)	Reference
NiO hollow microsphere	~2390	0.00167–6.87	0.53	3	[25]
c-Ni(OH) ₂ HR ^a	1569	0.002–3.8	0.6	10	[16]
Ni NP/SMWNTs ^b	1438	0.0001–1	0.5	3	[28]
Ni-CNT	1384.1	0.005–2	2	3	[48]
NA/NiONF-rGO/GCE ^c	1100	0.002–0.6	0.77	5	[49]
NiNWAs ^d	1043	0.0005–7	0.1	<10	[21]
Ni-SWCNTs	907	0.001–0.9	0.3	2	[50]
NiCFP ^e	420	0.002–2.5	1	5	[51]
Platelet-like Ni(OH) ₂	202	0.05–23	6	5–7	[52]
Ni-Ti-O NTs	83	2–200	0.13	10	[53]
5% NiO@Ag NWs ^f	67.51	0–1.28	1.01	7	[54]
Ni/Al LDH	24.45	up to 10	5	4	[27]
GNS/NiO/DNA ^g	9	0.001–8	2.5	8	[55]
Ni powder/CCE	0.04	0.0005–5	0.1	<1	[56]
Ni(OH) ₂ /TiO ₂	192	0.03–14	8	<1	Present work

^a Chemical bath deposited hollow Ni(OH)₂ nanorod arrays.

^b Nickel nanoparticles loaded straight multi-wall carbon nanotubes.

^c Reduced graphene oxide, NiO nanofibers and Nafion modified glassy carbon electrode.

^d Ni nanowire arrays.

^e Ni nanoparticle-loaded carbon nanofiber paste electrode.

^f 5% Ag nanoparticles coated NiO nanowires.

^g DNA-dispersed graphene nanosheet/NiO hybrids deposited GCE.

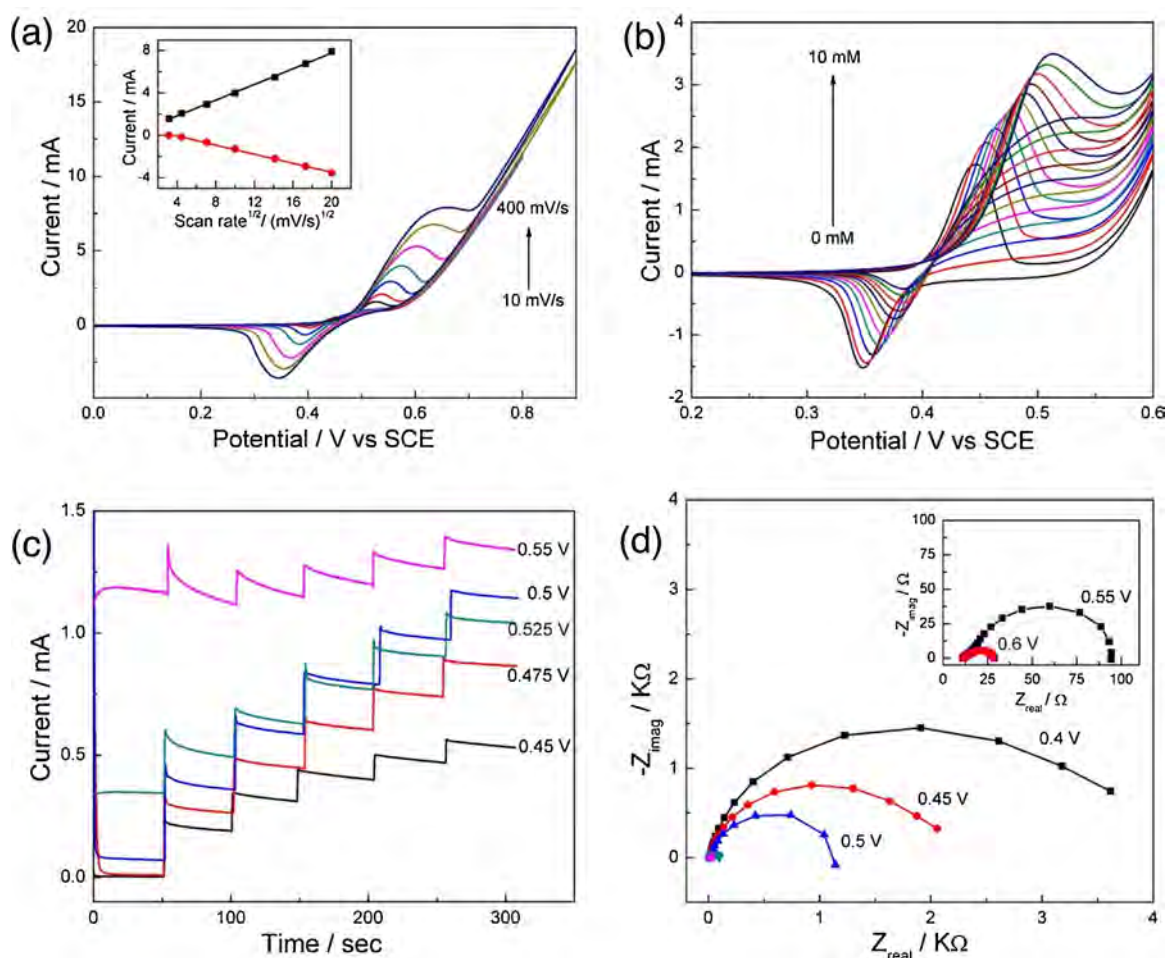


Fig. 4. (a) Cyclic voltammograms (CV) of the Ni(OH)₂/TiO₂ electrode at different scanning rate ranging from 10 to 400 mV/s in 0.1 M NaOH with addition of 5 mM glucose. The inset shows the linear dependence of the anodic and cathodic peak currents on the square root of the scanning rate. (b) CVs of the Ni(OH)₂/TiO₂ electrode in 0.1 M NaOH in the absence (0 mM) and presence of glucose varying from 1 to 10 mM at a scanning rate of 50 mV/s. (c) Amperometric response of the Ni(OH)₂/TiO₂ electrode at different potentials from 0.45 V to 0.55 V versus SCE upon successive addition of 1 mM glucose in 0.1 M NaOH. (d) Electrochemical impedance spectroscopy (EIS) results acquired from the Ni(OH)₂/TiO₂ electrode at different AC potentials in 0.1 M NaOH containing 5 mM glucose. The applied AC frequency range is 0.1 Hz–100 kHz and the probe amplitude is 5 mV.

prepared Ni(OH)₂/TiO₂ electrodes towards 5 mM glucose and the RSD is 5.53%.

The reliability of the Ni(OH)₂/TiO₂ electrode in routine analysis is demonstrated by measuring the glucose concentration in serum samples using a calibration curve and standard addition method. As shown in Table S1, the results are in good agreement with those obtained from a commercial GOx-based glucose meter (OneTouch, Life Scan, USA). Moreover, after addition of the standard glucose solution, the recovery is in the range of 95.5–104.3% indicative of practical feasibility.

3.6. Long-term stability

Another critical requirement for non-enzymatic glucose sensing is the long-term stability. The Ni(OH)₂/TiO₂ and Ni(OH)₂ electrodes are evaluated by monitoring the current response to 5 mM glucose every five days. When not in use, they were stored in air under ambient conditions. As can be seen in Fig. 5(d), the Ni(OH)₂ electrode shows large fluctuations during 30 days. In comparison, the sensitivity of the Ni(OH)₂/TiO₂ electrode only degrades gradually and after 30 days, 94% of the initial current response is retained signifying good long-term stability. This can be attributed to the protective effects rendered by the surface TiO₂ shown in Fig. 3(a). This stable TiO₂ not only protects the underlying metallic Ni from

further oxidation, but also stabilizes the formed Ni(OH)₂ and prevents its possible leakage which can undermine the sensitivity [33,57].

4. Conclusion

A one-step method to fabricate a non-enzymatic glucose sensor on NiTi alloy *in situ* by potential cycling in a concentrated alkaline solution is described. The electrode delivers good performance in amperometric detection of glucose including short response time because of fast electron transfer between the active surface species and underlying electrode. TiO₂ on the surface widens the linear range and produces excellent long-term stability. This simple and effective technique can be readily extended to the preparation of other transition-metal-based glucose biosensors.

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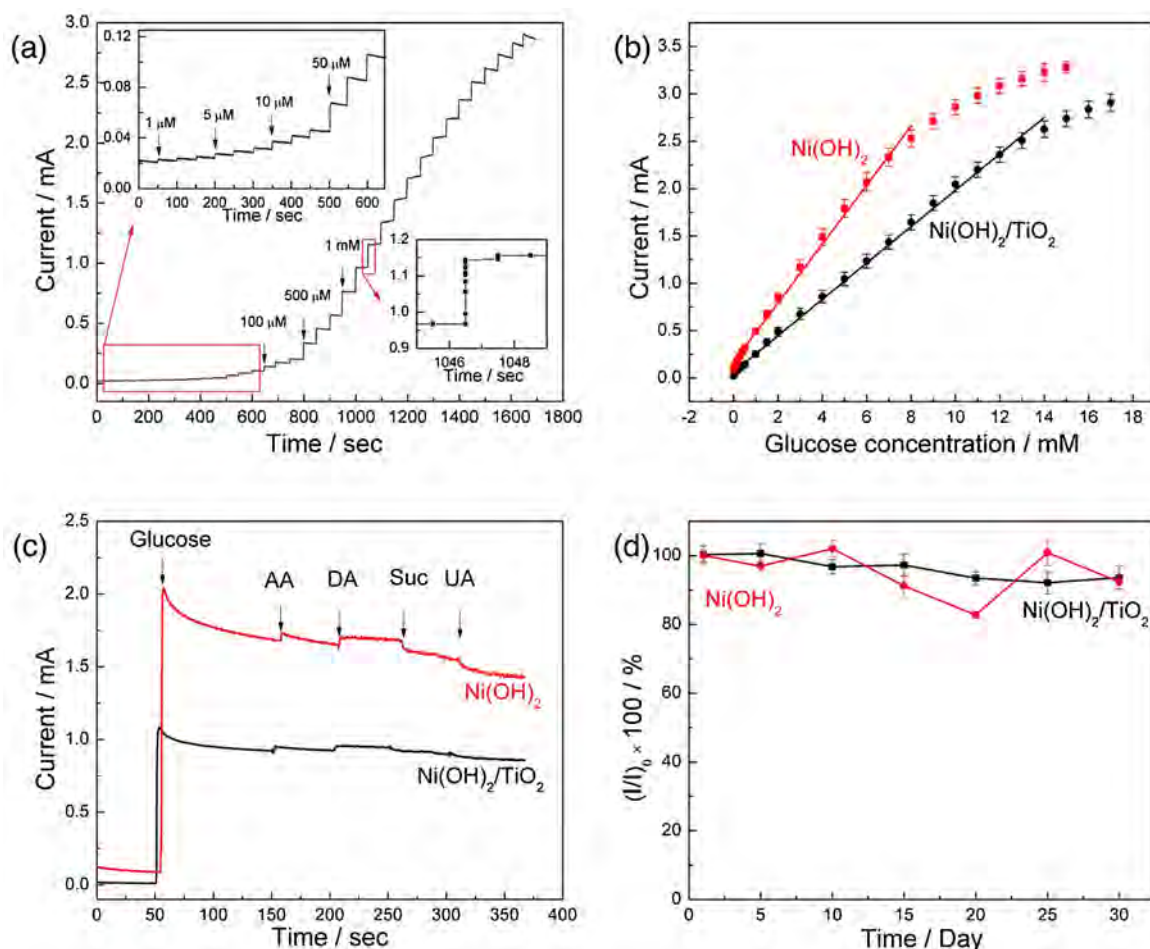


Fig. 5. (a) Amperometric responses of the Ni(OH)₂/TiO₂ electrode to various concentrations of glucose in 0.1 M NaOH at 0.5 V versus SCE. The left inset exhibits partial amplification and the right inset shows the response time of the Ni(OH)₂/TiO₂ electrode after addition of 1 mM glucose. (b) Calibration curve of the response current versus glucose concentration according to the curve shown in (a) for Ni(OH)₂/TiO₂ and Fig. S7 for Ni(OH)₂. The error bars indicate standard deviations for triplicate measurements at each glucose concentration. (c) Interference test performed on the Ni(OH)₂/TiO₂ and Ni(OH)₂ electrodes in 0.1 M NaOH at 0.5 V versus SCE with successive addition of 5 mM glucose, 0.1 mM ascorbic acid (AA), 0.1 mM dopamine (DA), 0.1 mM sucrose (Suc), and 0.1 mM uric acid (UA). (d) Normalized sensitivity of the Ni(OH)₂/TiO₂ and Ni(OH)₂ electrodes stored under ambient conditions towards 5 mM glucose monitored every five days amperometrically for 30 days. The error bars indicate standard deviations of three measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2016.03.122>.

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