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SHORT COMMUNICATION

Porous Ni_3N nanosheet array as a catalyst for nonenzymatic amperometric determination of glucose

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Abstract

A glassy carbon electrode was modified with an array of porous Ni_3N nanosheets (Ni_3N NA) and studied for its use in non-enzymatic electrochemical detection of glucose. The morphology and structure of the Ni_3N NA were characterized by scanning electron microscopy and X-ray diffraction. Electrochemical studies demonstrated that the Ni_3N NA acts as an efficient catalyst for the electro-oxidation of glucose at pH 13, best at a working voltage of 0.55 V (vs. Ag/AgCl). Figures of merit include (a) high sensitivity (39 $\mu A \cdot mM^{-1} \cdot cm^{-2}$), (b) a low limit of detection (0.48 μM), and (c) a linear range that extends from 2 μM to 7.5 mM. The sensor was applied to the determination of glucose levels in human serum, and satisfactory results were obtained.

Keywords Ni_3N · Non-enzymatic sensor · Electrocatalytic activity · Amperometry · Human serum

Introduction

Sensitive and effective determination of blood glucose concentrations is of great importance for diagnosis and management of diabetes [1]. To date, a variety of analytical approaches have been studied for glucose detection, such as colorimetry [2, 3], Raman scattering [4, 5], fluorescence [6] and electrochemistry [7, 8]. Among these methods, electrochemistry has been demonstrated to be a promising detection technique due to its merits of good sensitivity, low cost and simple instrumentation [9–14]. A number of electroactive materials have been investigated for their applications in non-enzymatic glucose sensing [15, 16]. These materials include metal oxides [17, 18], metal phosphates [19], nitrides [20, 21], chalcogenides [7], metallic cluster [22] and metal-organic framework (MOF) [23].

Nickel nitride based nanomaterials have attracted increasing attention due to their good electrical conductivity [24]. Thus, they have been utilized for gas sensing [25, 26] and in the field of catalysis, such as hydrogen evolution reaction (HER) [27] and oxygen evolution reaction (OER) [28]. The high HER catalytic activity of transition metal nitrides is owing to their distinctive electronic structure that enables appropriate adsorption between the surface of nitrides and the protons during the catalytic processes [29].

Herein, we synthesized porous Ni_3N nanosheets array (NA) and tested its performance towards nonenzymatic electrochemical glucose detection. Sensitive detection of glucose was realized in alkaline electrolyte with good selective and fast response. The electrochemical sensor was also successfully applied to the detection of glucose in human serum.

Experimental

Materials and apparatus

$Ni(NO_3)_2 \cdot 6H_2O$ was purchased from Aladdin Ltd. (Shanghai, China, http://www.aladdin-e.com/). Ammonium fluoride (NH_4F) and urea and nitric acid (HNO_3) were purchased from Beijing Chemical Works (Beijing, China, http://bjchem.company.weiku.com/). Glucose and sodium hydroxide (NaOH) were obtained from Sinopharm Chemical

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Reagent Co. Ltd. (Shanghai, China, http://en.reagent.com.cn/). For real sample analysis, the blood samples were obtained from the Second Xiang-ya Hospital attached to Central South University (http://www.xyeyy.com/). All other reagents were of analytical grade and ultrapure water (≥18.2 MΩ cm) was used throughout the experiments.

Scanning electron microscopy (SEM) images were collected on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. X-ray diffraction (XRD) patterns were recorded from a D8ADVANCE (Bruker, Germany) X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å).

All the electrochemical experiments were performed on a CHI-650D electrochemical workstation (Shanghai CH Instruments Co., China), with Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum wire as the auxiliary electrode, and a glassy carbon electrode (GCE) as the working electrode.

Synthesis of porous Ni_3N NA

In a typical procedure, 4.5 mM $Ni(NO_3)_2{\cdot}6H_2O$, 8 mM NH_4F and 20 mM urea were dissolved in 80 mL distilled water and stirred to form a clear solution. Then the above solution and a piece of cleaned Ti metal substrate (2 cm × 3 cm) were transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 6 h. After the autoclave cooled down naturally, the resulting Ti metal substrate was taken out and washed with distilled water and ethanol, followed by drying 2 h at 60 °C to obtain $Ni(OH)_2$ NA. To prepare porous Ni_3N NA, the Ti metal substrate with $Ni(OH)_2$ NA grown on it was placed in a tube furnace, and heated at 380 °C in a furnace for 3 h in NH_3 atmosphere, and then naturally cooled to ambient temperature under NH_3. Finally, the black Ni_3N NA was collected by scraping from the Ti metal substrate for further characterization.

Electrochemical characterization of the porous Ni_3N NA modified electrode

The GCE (3.0 mm in diameter) was first polished successively with 0.3 and 0.05 μm alumina slurry, followed by sonication in ethanol and ultrapure water. Next, the electrode was dried under blowing nitrogen. Then, 7.5 μL of 1% (*w*/*v*) chitosan water solution containing Ni_3N NA (3 mg mL^{-1}) was deposited on the surface of GCE and dried overnight under room temperature.

The amperometric response of the Ni_3N NA modified electrode to glucose was recorded through successively adding glucose to a 20 mL 0.1 M NaOH solution with stirring at a constant speed of 60 rpm at potential of 0.55 V. The current response of the electrode at 0.55 V was collected for the calibration plot.

Results and discussion

Choice of materials

Ni_3N NA was selected as a new catalyst towards nonenzymatic electrochemical detection of glucose. The Ni_3N NA has large specific surface area, good catalytic activity and can be synthesized in large scale. The Ni_3N NA was dispersed into chitosan solution and then casted onto electrode. The Ni_3N NA can be well dispersed into chitosan solution and the chitosan layer can prevent the leakage of the Ni_3N NA from the electrode surface and improve the stability of the electrode.

Characterization of the synthesized materials

The Ni_3N NA was synthesized from $Ni(OH)_2$ NA precursor through NH_3 nitridation. Figure 1a shows the X-ray diffraction (XRD) patterns of the porous Ni_3N NA. The porous Ni_3N NA presents six peaks at 38.9°, 42.1°, 44.5°, 58.5°, 70.6° and 78.4°, corresponding to the (110), (002), (111), (112), (300) and (113) planes of Ni_3N, respectively (JCPDS no.10–0280) [30]. Figure 1b and c show the scanning electron microscopy (SEM) images of the porous Ni_3N NA, which indicates that the porous Ni_3N NA with a well-preserved morphology is successfully synthesized.

Electrochemical detection of glucose

The Ni_3N NA modified electrode was characterized by cyclic voltammetry (CV). Figure 2 present the CVs of bare GCE electrode in the absence and presence of 10 mM glucose, and porous Ni_3N NA modified GCE electrode in the presence of 0 mM, 3 mM and 10 mM glucose in 0.1 M NaOH solution at scan rate of 20 mV s^{-1}. For bare GCE electrode in the absence and presence of 10 mM glucose, no redox peaks are observed, which indicate bare electrode has no electrocatalytic activity toward glucose oxidation. However, for porous Ni_3N NA modified GCE electrodes in the presence of 0 mM, 3 mM and 10 mM glucose in alkaline solution, an obvious increase of current is observed, which is ascribed to the oxidation of glucose at the porous Ni_3N NA modified GCE electrodes.

The chronoamperometric study was carried out to evaluate the detection sensitivity of the porous Ni_3N NA modified electrode for glucose at a potential of 0.55 V. The result shows that with the addition of 250 μM of glucose, the response current of the porous Ni_3N NA modified electrode is increased steadily (Fig. 3). The steady-state current can be achieved within 5 s, demonstrating its rapid electrochemical response to glucose. However, with the addition of the same concentrations of glucose, there was no apparent current observed on bare GCE.

The calibration curve of our glucose sensor is shown in Fig. 4, which gives a linear dependence on glucose concentration in the range of 2 μM to 7.5 mM (R^2 = 0.998). The detection limit and

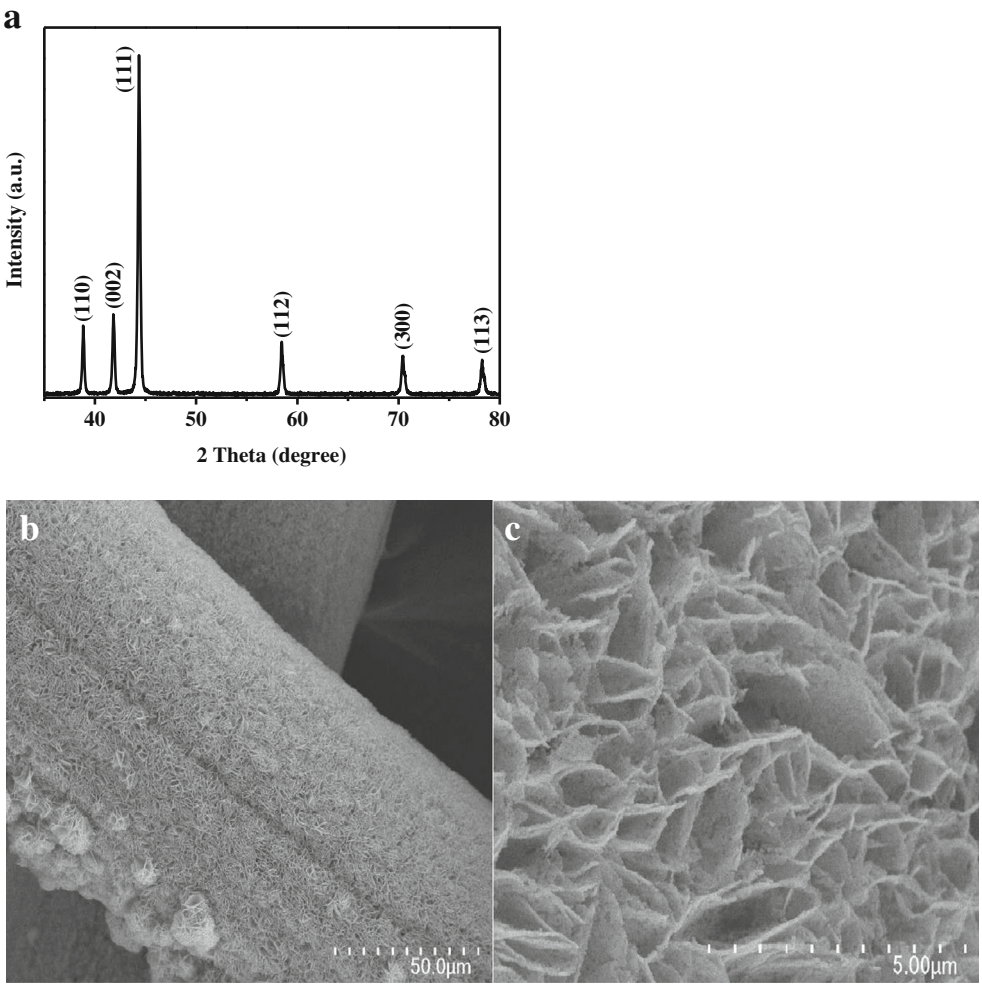

Fig. 1 **a** XRD patterns for the porous Ni_3N NA. **b** Low and (**c**) high magnification SEM images of the porous Ni_3N NA

sensitivity are calculated as 0.48 μM (based on SNR of 3) and 39.02 μA mM^{-1} cm^{-2}, respectively.

Table 1 shows the compare of the analytical performances of the Ni_3N NA modified electrode with literature reported nonenzymatic glucose sensors. It is obvious that

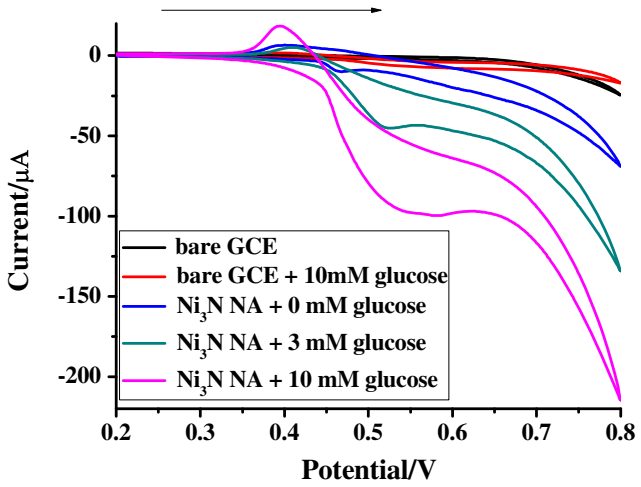

Fig. 2 Cyclic voltammetry curves (CVs) of bare GCE electrodes in the absence and presence of 10 mM glucose, and porous Ni_3N NA modified GCE electrodes in the presence of 0 mM, 3 mM and 10 mM glucose in 0.1 M NaOH solution at scan rate of 20 mV/s. The arrow indicated the scan direction

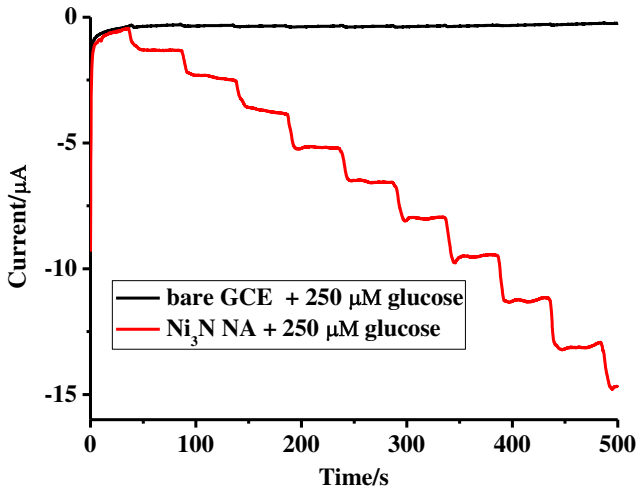

Fig. 3 Amperometric response of bare GCE electrodes and porous Ni_3N NA modified GCE electrodes to successive additions of 250 μM glucose at an applied potential of 0.55 V

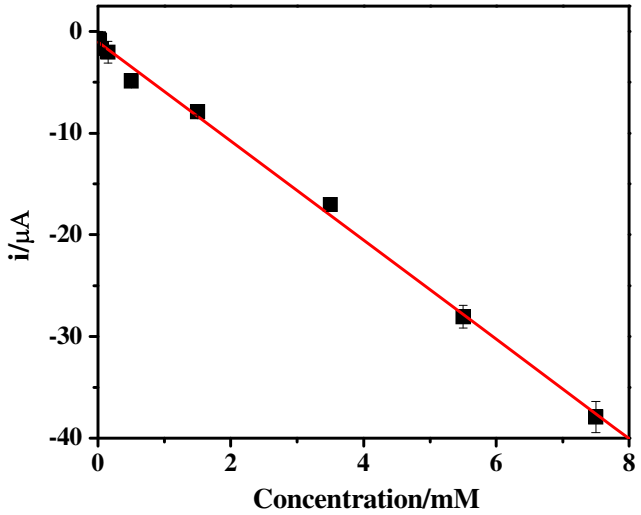

Fig. 4 Calibration plot of the porous Ni_3N NA modified GCE electrodes to different concentrations of glucose. Working potential: 0.55 V

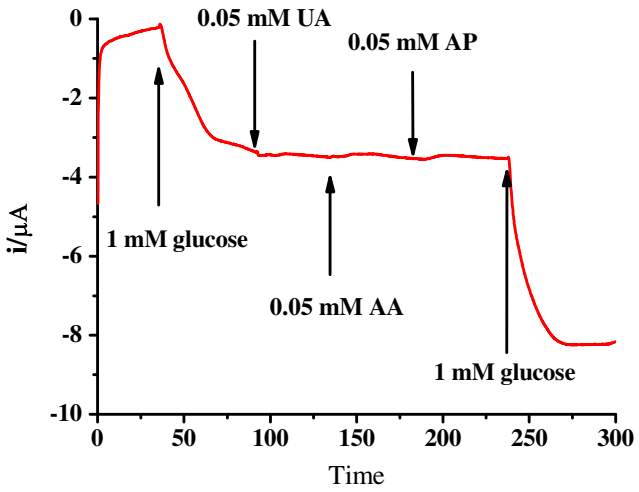

Fig. 5 Amperometric responses of the porous Ni_3N NA modified GCE electrodes to successive addition of 1 mM glucose, 0.05 mM UA, AA and AP. Detection potential at 0.55 V

the performance of the porous Ni_3N NA modified GCE electrodes is comparable or even better than the previous literature reports.

For accurate detection of glucose in real samples, it is crucial to eliminate the interference of potential electroactive species that commonly present in the blood sample. These species include ascorbic acid (AA), uric acid (UA) and acetaminophen (AP). As in physiological condition, the concentration of glucose (3–8 mM) is much higher than the concentration of these species (<0.5 mM), the sensitivity of the Ni_3N NA modified electrode to 1 mM glucose, 0.05 mM AA, UA and AP were studied [22]. The amperometric responses of the porous Ni_3N NA modified electrode at 0.55 V in 0.1 M NaOH with successive addition of 1 mM glucose, 0.05 mM UA, 0.05 mM AA and 0.05 mM AP are shown in Fig. 5. Compared to the addition of glucose, there are no distinctive current changes after the addition of the above interferences, indicating good selectivity of the electrode and the electrode can be further applied for selective detection of glucose in blood samples [22].

The reproducibility of the porous Ni_3N NA modified electrode was studied by testing 2 μM of glucose independently three times. The relative standard deviation (RSD) of the testing results is 0.14%, indicating good reproducibility of the sensor.

Real sample analysis

The potential of the porous Ni_3N NA modified electrode for real sample analysis was checked by detection of glucose level in the human serum samples. Serum samples were analyzed by the hospital and then by our sensor. From Fig. 6, it can be seen that the responses of the sensor to the same concentrations of glucose in human serum and in standard buffer are rather close, which indicate that the porous Ni_3N NA modified electrode can be utilized for practical sample testing with good accuracy and precision.

Table 1 Comparison of different modified electrodes for glucose determination

Materials	Linear range (mM)	Detection limit (μM)	References
Mixed copper and cobalt oxides	0.005–0.57	0.5	[31]
bulk Ni	0.002–3	13	[32]
PdCuPt Nanocrystals	1–10	1.29	[33]
$Ni(OH)_2$-PEDOT-rGO	0.002–7.1	0.6	[34]
Flower-like CuO	0.04–2	2.5	[35]
Nickel hydroxide	0.0005–0.0115	0.12	[36]
Ni_3N NA	0.002–7.5	0.48	This work

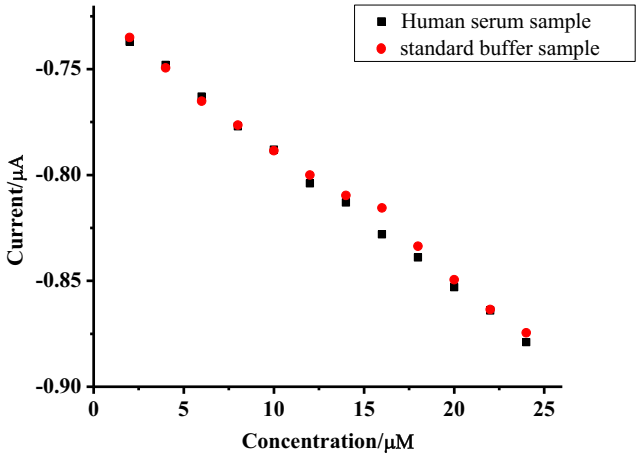

Fig. 6 Compare the responses of the sensor to the same concentrations of glucose in human serum sample (black) and in standard sample (red)

Conclusion

In summary, porous Ni_3N NA was synthesized and proved as an efficient catalyst for glucose electro-oxidation under alkaline conditions. This glucose sensor exhibits good sensing performances for analyzing glucose level in human serum. Our present study not only provides an attractive low-cost material for high efficiency glucose detection, but opened new opportunity to explore the porous Ni_3N NA modified electrode as electrochemical sensor for analytical applications. However, the major limitation of the present method is the performance of the test in strong alkaline NaON solution, which may needs improvement.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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