Colloids and Surfaces A: Physicochem. Eng. Aspects 509 (2016) 252–258

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Non-enzymatic glucose sensor based on facial hydrothermal synthesized NiO nanosheets loaded on glassy carbon electrode

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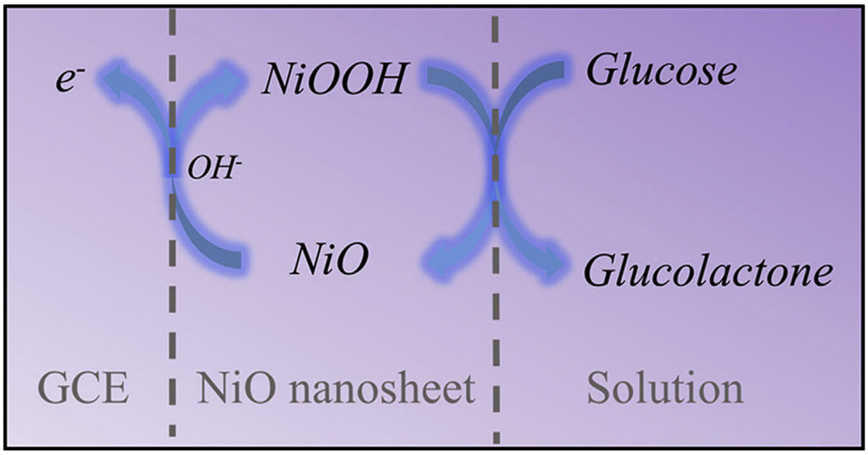
HIGHLIGHTS

- Non-enzymatic sensory of glucose through two dimensional NiO was proposed.
- NiO nanosheets were hydrothermally synthesized and loaded on glassy carbon electrode.
- NiO nanosheets exhibited a large detection range and high sensitivity for glucose.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 July 2016
Received in revised form 26 August 2016
Accepted 28 August 2016
Available online 30 August 2016

Keywords:
Nanosheet
Electrochemical
Non-enzymatic
Glucose

ABSTRACT

In this work, NiO nanosheets have been successfully synthesized *via* a facial hydrothermal route and it was found to be an excellent catalyst for non-enzymatic glucose sensory application. The NiO nanosheets in *fcc* structure were examined by transmission electron microscopy (TEM), field emission scanning electron microscopy(FESEM), X-ray diffraction (XRD) and selected area electron diffraction (SEAD). The thickness of NiO nanosheets were found to be 40–50 nm. This catalyst was then dropcasted on a glassy carbon electrode (GCE) for glucose sensory purposes. The electrochemical measurements were undertaken using both voltammetric method and amperometric method. The former offer a wide concentration range for glucose (up to 2.2 mM) but with relatively low sensitivity, whereas the latter showed excellent sensitivity with 400.29 μA mM^{-1} cm^{-2} and 1 μM detection limit. Thus the as-synthesized NiO nanosheets demonstrated potential application in non-enzymatic sensory of glucose.

1. Introduction

The measurement of glucose is of great importance in various fields, such as environmental monitoring, clinical diagnostics

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http://dx.doi.org/10.1016/j.colsurfa.2016.08.076
0927-7757/

and food industry [1–3]. High level of glucose in blood may lead serious diseases such as diabetes mellitus [4,5]. In 2014, more than 400 million people around the world are afflicted by diabetes mellitus and this number is still increasing [6]. Tremendous efforts have been made for glucose detection using varies detection methods, including chromatography [7,8], colorimetry [9], electrochemiluminescence [10], fluorescence [11], chemiluminescence [12], spectrophotometric assay [13] and electrochemical detection [14–16]. Compare to other methods, the electrochemical technique has offered promising advantages, such as easy construction, low cost, high sensitivity, good selectivity and ease of operation [17], since its first introduction by Clark and Lyons in 1962 [18]. Hence commercial handheld glucose sensors are normally designed based on electrochemical detection methods [19]. Such sensor uses glucose oxidase (GO*x*) as catalyst, in which glucose can be oxidized *via* an enzymatic catalytic reaction in the presence of oxygen and the product can be electrochemically oxidized to acquire the current response [4]. Although enzymatic electrochemical biosensors are commercially produced since enzyme offers excellent sensitivity and selectivity [20,21], such glucose biosensors often suffer from some drawbacks such as high cost, short-term stability, sensitive to temperature, pH, *etc* [22]. Besides, the immobilization of enzymes also results in poor stability and complicated fabrication procedures for the sensors [23].

Transition metal oxide (TMO) nano-materials were widely investigated to replace enzymes in glucose biosensors, namely non-enzymatic electrochemical biosensors [24], such as NiO [25,26], CuO [27,28], Co_3O_4 [29], CoO [30] and MnO_2 [31]. TMO catalyst can be applied for electrochemical determination of glucose due to their low cost, easy to synthesize and long-term stability. Furthermore, TMO offers better electrochemical activity compare to GO*x* thanks to their enhanced conductivity and low redox potential. Such biosensors have been developed decades to improve the sensitivity and selectivity to glucose.

Among the TMOs, NiO shows great sensitivity to glucose, together with excellent stability and low cost [32]. Synthetic approaches to prepare nano-sized NiO involves electrochemical deposition [33], atomic layer deposition [34], magnetron sputtering deposition [35], hydrothermal synthesis [36,37], *etc*. Among them, hydrothermal methods were widely used due to its facial synthetic procedure. In this work, well distributed NiO nanosheets have been successfully prepared *via* a facial hydrothermal method followed by annealing at 400 °C. And it was further applied for sensory means through electrochemical detection of glucose.

2. Material and methods

2.1. Material

All the reagents used in the experiment were of analytical grade and were used without further purification. $Ni(CH_3COO)_2{\cdot}4H_2O$ was purchased from Shanghai Aladdin Chemistry Co. Ltd., China. Urea and ethanol were bought from Sinopharm Chemical Reagent Co. Ltd.

2.2. Apparatus

The structures of the samples were examined with powder X-ray diffraction (XRD) by using a Philips X'Pert diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). Transmission electron microscopy (TEM) and high resolution transmission electron microscope (HRTEM) analysis were obtained on a JEM-2100UHR transmission microscope (JEOL, Japan) operated at 200 kV. Scanning electron microscopy (SEM) were conducted with a Hitachi S-4800 field emission scanning electronic microscopy (FESEM). Electrochemical measurements were performed on a CHI 660E electrochemical workstation (CH instruments, Shanghai) with standard three electrode configuration. A glassy carbon disc electrode (3 mm in diameter) serves as working electrode. A saturated calomel electrode acts as reference electrode and a Pt plate as the counter electrode.

2.3. Synthesis of NiO nanosheets

In a typical synthesis, 1 mmol of $Ni(CH_3COO)_2{\cdot}4H_2O$ and 4 mmol of urea were dissolved into 30.0 mL of deionized (DI) water. The mixture was kept at an intense ultrasonic treatment for a few minutes to form a light green solution and then transferred to a 50 mL Teflon-lined stainless steel autoclave and kept at 150 °C for 6 h. The as-synthesized product was centrifuged and washed several times with deionized water and absolute ethanol before vacuum drying at 60 °C. Finally, the product was annealed at 400 °C for 2 h in air with the heating rate of 2 °C/min to obtain the NiO nanosheets.

2.4. Preparation of NiO/GCE and electrochemical determination of glucose

3 mg of NiO nanosheets was dissolved in 1 mL ethanol with 0.5% Nafion. The mixture was sonicated for 20 min to obtain a homogeneous black ink. Glassy carbon electrode (GCE) was polished with 0.25 μm Al_2O_3 slurry on polishing cloth before each electrochemical experiment, followed by sonication in ethanol, 6 M HNO_3 and water subsequentially. Then 3 μL of the aforementioned ink was dropcasted on GCE and left to dried in air. The modified electrode was then ready for electrochemical measurements. All the electrochemical measurements were carried out in 0.1 M NaOH electrolyte solution.

3. Results and discussion

3.1. Structural characterization of NiO nanosheets

TEM and SEM images have been taken primarily to reveal morphology of the as-prepared NiO samples (Fig. 1). As shown in Fig. 1a, NiO affords flower-like morphology, which is consisted of large number of nanosheets with an average thickness ranging from 40 nm to 50 nm. High resolution TEM shows the lattice spacing of 0.247 nm, consisting with the (111) crystal planes of face-centered cubic (*fcc*) NiO. The SEM image (Fig. 1b) shows that the NiO nanosheets are uniformly distributed, which is ideal for electrocatalytic detection purposes. SEM image was also taken for $Ni(OH)_2$ nanosheets (Fig. 1d), which was obtained prior to the 400 °C calcination process. Well defined circular $Ni(OH)_2$ nanosheets can be observed. The size of $Ni(OH)_2$ nanosheets were similar to that of the NiO nanosheets, but with the circular shape rather than the "flower-like" shape. Therefore, it is assumed that a certain degree of aggregation happened for $Ni(OH)_2$ during the annealing process, leading to the formation of flower-like NiO consisting of nanosheets.

Fig. 2a shows the XRD patterns for the intermediate $Ni(OH)_2$ and final NiO nanosheets. The diffraction peaks at 37.3°, 43.2° and 62.9° can be indexed to the (111), (200) and (220) crystal planes for *fcc* NiO (JCPDS 73-1523). The data was also comparable to literatures and no other peaks were observed, indicating brilliant purity of the synthesized NiO nanosheets. XRD data was also acquired for $Ni(OH)_2$ precursor before calcination in order to examine its structure and purity. The 2θ angles were found at 12.5°, 25.3°, 33.4°, 36.7° and 59.6° as indexed to the (003), (006), (101), (015) and (110) crystal planes of $Ni(OH)_2$, respectively [38]. Compare with the two XRD patterns for NiO and $Ni(OH)_2$, no trace of $Ni(OH)_2$ peaks were observed in NiO data, indicating complete conversion