Electrochimica Acta 109 (2013) 532–535

Contents lists available at ScienceDirect

Electrochimica Acta

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

A novel nonenzymatic electrochemical glucose sensor modified with Ni/Al layered double hydroxide

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ARTICLE INFO

Article history:
Received 19 June 2013
Received in revised form 2 August 2013
Accepted 3 August 2013
Available online 11 August 2013

Keywords:
Ni/Al layered double hydroxide
Glucose
Sensor
Electrochemical

ABSTRACT

A novel cheap and simple enzymeless glucose sensor, based on flower-shaped Ni/Al layered double hydroxide (LDH) modified glassy carbon electrode (GCE), has been successfully fabricated. Cyclic voltammetry (CV) revealed that Ni/Al-LDH nanoflowers exhibited direct electrocatalytic activities similar to that found in natural peroxidases for the oxidation of glucose in an alkaline solution. The very good linear relationship toward glucose can be obtained in two regions: 1–100 μM and 0.5–21 mM, with a detection limit of 0.11 μM. The proposed nonenzymatic sensor can be used for the assay of glucose in real samples. In addition, the glucose sensor also exhibited excellent stability, good reproducibility, and high selectivity.

1. Introduction

Layered double hydroxides (LDHs), well known as anionic or hydrotalcite-like clays consist of positively charged edge sharing octahedra forming brucite-like host layers. Net positive charges on the layers are balanced by exchangeable anions intercalated between the sheets [1–4]. Their remarkable features such as the layered structure, large surface area and anion exchange capability make them attractive as electrode surface modification materials applied in electrochemistry [5–7].

Since 1987, many publications have reported on the use of synthetic LDHs for the modification of electrodes [8]. Among natural and synthetic clays, LDHs compounds are particularly interesting as electrode surface modifiers. These modified electrodes have been proposed as amperometric or potentiometric sensors. Among these LDHs, Ni-based LDHs are of particular interest due to their use in heterogeneous catalysts to glucose [9,10].

Compared to spherical nanoparticles, well-aligned 2-D nanosheet film on conductive substrates are more promising in biosensor development, because the interconnected structure is especially efficient for the transport of electrons and its high surface area-to-volume ratio could effectively increase the electrode–electrolyte contact area.

The detection of glucose is very important in various fields including clinical chemistry, biochemistry, environmental and food chemistry, because glucose is the product of the reactions catalyzed by a large number of oxidases. Many effective methods have been applied for the determination of glucose. Among these methods, most studies on this subject involved the use of the enzyme glucose oxidase [11,12]. These however, suffer from the chemical and thermal instabilities due to the intrinsic nature of enzymes. To resolve this issue, many efforts have been tried for the direct determination of glucose at enzyme-free electrodes [13–15].

In this paper, we constructed a novel hybrid film of Ni/Al-LDH/Nafion (Nf) on a GCE as a catalytic layer for glucose detection, taking advantage of flower-shaped Ni/Al-LDH with great adsorption capacity and microscopic network structure of Nf. It is surprising to discover that Ni/Al-LDH exhibits a remarkable electrocatalytic activity for the oxidation of glucose without loading any enzymes. In Ni/Al-LDH nanoflowers, the Ni^{2+} cations play an essential role in the electrocatalytic detection of glucose. The good analytical performance, low cost and straightforward preparation method made Ni/Al-LDH promising for the development of a nonenzymatic glucose sensor and a forseable applied foreground in medicine, biotechnology and environmental chemistry.

2. Experimental

2.1. Reagents and apparatus

All chemicals including $Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, urea, glucose, and NaOH were of analytical grade and were used as

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http://dx.doi.org/10.1016/j.electacta.2013.08.017

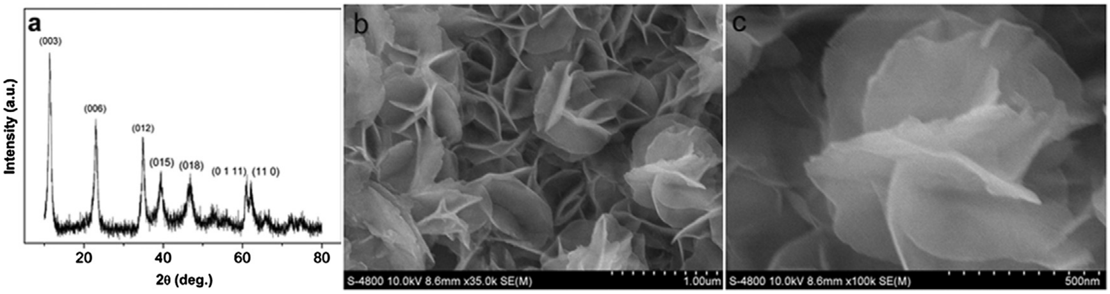

Fig. 1. (a) XRD pattern and (b and c) SEM images of the as-prepared product.

received without further purification. All aqueous solutions were prepared in distilled water. Glucose solutions with different concentrations were daily prepared and stored overnight to reach mutarotational equilibrium before use.

All electrochemical measurements were performed using CV with electrochemical analyzer (CHI 660C, CH Instruments). A conventional three-electrode system was adopted. The working electrodes were modified GCE, the reference electrode was an Ag/AgCl (sat. KCl) electrode and the counter electrode was platinum wire. The products were characterized with a Hitachi S-4800 scanning electron microscope (SEM) and X-ray powder diffraction (XRD) (Bruker D-8 Avance, Cu K_α radiation, 1.5418 Å).

2.2. Synthesis

The Ni/Al-LDHs were prepared by homogeneous precipitation through urea hydrolysis. In brief, a solution containing 0.005 mol amount of $Ni(NO_3)_2 \cdot 6H_2O$ and 0.0025 mol of $Al(NO_3)_3 \cdot 9H_2O$ in 50 mL of deionized water was prepared. 0.0175 mol urea was added to the solution. The as-obtained solution was heated at 100 °C under continuous magnetic stirring for 9 h in a flask. Afterwards, the prepared suspension was heated at 94 °C for 14 h without stirring. The precipitate was harvested by centrifugation then rinsed with deionized water and ethanol, and dried in air for further characterizations.

2.3. Electrode modification

Prior to the modification, the GCE surface was carefully polished to a mirror-like surface with 0.05 μm alumina powders and then sonicated successively in ethanol and deionized water for 5 min, separately. Secondly, Nf was diluted with ethanol to 2%. 20 mg Ni/Al-LDHs were dispersed in 3 ml Nf solution. Then, 20 μl of Ni/Al-LDHs/Nf solution (6.66 mg/ml) was dropcasted on the surface of GCE and dried in air for further use.

3. Results and discussion

3.1. Characterization of the Ni/Al-LDH

Fig. 1a depicts the XRD pattern of the Ni/Al-LDH. All diffraction peaks of the products can be indexed as Ni/Al-LDHs (PDF No. 15-0087). The typical morphology of the Ni/Al-LDH nanoflowers, as observed by SEM, is shown in Fig. 1b and c at different magnifications. As can be seen, the nanoflower consists of many interconnected nanosheets with the thickness of 10–20 nm and lateral size of about 600 nm. Cherishing the merits of high specific area and structural stability, Ni/Al-LDH modified electrode surfaces may limit the denaturing adsorption to a lesser extent and are also convenient for the electron transport and penetration of electrolyte.

3.2. The voltammetric detection of glucose on the Ni/Al-LDH/Nf/GCE

Fig. 2(A and B) depicts the typical CVs obtained at the GCE modified with Ni/Al-LDHs/Nf in 0.1 M NaOH solution in the absence and presence of glucose. When glucose was injected to the solution, compared with the system without glucose (0 μM), an obvious increase of the reduction peak current was observed (1–100 μM). Also, along with the increase of glucose concentration from 1 μM to 0.1 mM, the reduction peak current is stronger. The cathodic current obviously increases which is due to the catalytic effect of the Ni^{3+}/Ni^{2+} redox couple for oxidation of glucose. The results further confirm that it is the Ni/Al-LDH plays a significant role in the electrocatalytic oxidation of glucose. The electro-oxidation mechanism is shown in Fig. 3, which can be explained by the following reactions [16]:

$$\text{LDH-Ni(II)} + \text{OH}_{\text{sol}}^{-} \rightarrow \text{LDH(OH}^{-}\text{)-Ni(III)} + e^{-} \qquad (1)$$

$$\text{LDH(OH}^{-}\text{)-Ni(III)} + \text{Glucose} \rightarrow \text{LDH-Ni(II)} + \text{Glucolactone} \qquad (2)$$

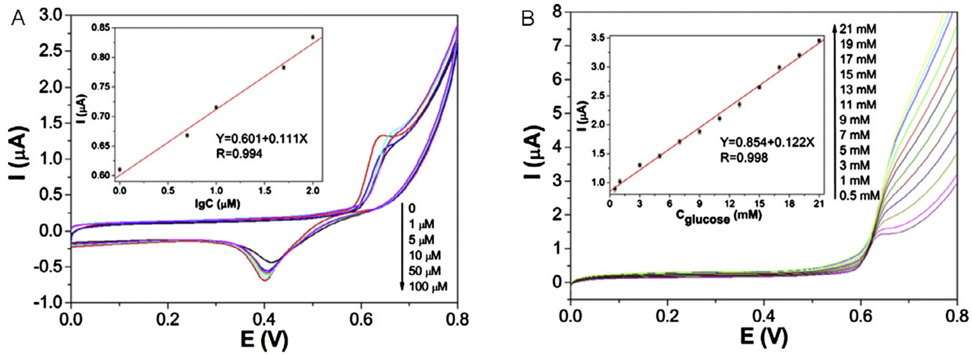

Fig. 2. CVs of the Ni/Al-LDH/Nf/GCE in 0.1 M NaOH solution with increasing glucose concentration from (A) 1 to 100 μM and (B) 0.5 mM to 21 mM of glucose at the scan rate of 0.05 V/s. Inset: The linear relationship between the catalytic current and glucose concentration.