

Electrodeposition of NiO_x/PANI Composite Film and its Catalytic Properties towards Electrooxidations of Polyhydroxyl Compounds

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ABSTRACT: Electrocodeposition of nickel oxide (NiO_x) and polyaniline (PANI) was conducted through cyclic voltammetric scans in an aqueous solution of NiSO₄ and aniline. Characterizations of the obtained NiO_x/PANI composite film by XRD and FTIR indicated that the film composed of NiO_x and PANI, in which nickel oxide was in the form of Ni₂O₂(OH). Ni(II)/Ni(III) redox couple appeared at 0.30 V versus SCE on the cyclic voltammogram (CV) of the composite film. Electrooxidations of glucose and fructose occurred

at the potential where nickel oxide existed in higher oxidation state. The anodic current densities at 0.46 V for the electrooxidations were linearly dependent on the concentration of polyhydroxyl compounds from 1 to 100 mM for glucose and 10 to 100 mM for fructose, respectively. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2260–2264, 2007

Key words: electrochemistry; inorganic materials; conducting polymers; composites

INTRODUCTION

Organic–inorganic composites have attracted considerable attention as they can combine the advantages of both components or offer special properties through modification each other.¹ Polyaniline (PANI) has been the subject of many studies due to its oxygen- and moisture-stability, and potential applications in many fields.² PANI can also provide good network for inorganic components and modify the latter.³ Nickel oxide has received considerable attention over the last few years due to its potential applications in the fields of electrochromics, electrocatalysis, supercapacitor, and etc.^{4–7} Therefore, the composition of nickel oxide and PANI may provide a new material with modified properties.

Electrocodeposition is an effective way to produce composite films with a large variety of tunable parameters and so the advantage of convenient film control. Anodic electropolymerization of aniline in acidic aqueous solutions is a convenient synthetic method for PANI.⁸ However, electrodeposition of oxide is scarcely conducted in low pH media. Thus, electro-

chemical syntheses of organic–inorganic composites based on PANI and oxides are very limited.³

Nickel oxide was reported to electrodeposite either potentiostatically at a fixed potential (0.7–1.2 V) or by potential cycling in potential range of 0–1.2 V versus SCE from Ni²⁺ at comparatively high pH.⁹ There is no report about the electrocodeposition of NiO_x and PANI, to the best of our knowledge. Recently, we demonstrated the electropolymerization of aniline in aqueous solutions of pH 2–12. Electroactive PANI was successfully obtained in the whole pH range studied.¹⁰ This provides an opportunity for PANI and nickel oxide to electrocodeposit and form an organic–inorganic composite film. In this article, electrocodeposition of NiO_x and PANI is conducted by cyclic voltammetric scans in a neutral aqueous solution. The organic–inorganic composite film obtained is characterized by X-ray diffraction (XRD) and FTIR spectroscopy. Electrocatalytic oxidations of some polyhydroxyl compounds are performed on the composite film.

EXPERIMENTAL

Electrochemical syntheses and electroactivities study

Aniline was distilled before use under vacuum. Other chemicals were of analytical grade and used as received. Electrochemical syntheses were performed on electrochemical analyzer system, CHI 660B on carbon cloth or ITO glass for XRD measurement. Potentials were reported versus SCE. Prior to electrodeposi-

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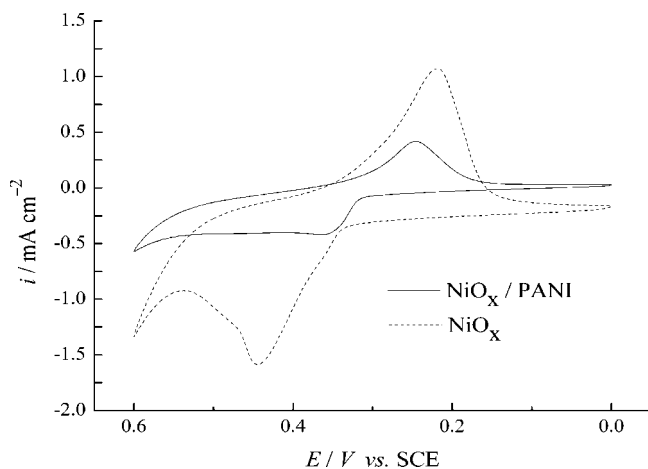


Figure 1 Cyclic voltammograms of NiO_x/PANI (solid line) and NiO_x (dash line) films in 1M NaOH; scan rate: 5 mV s⁻¹.

tion, carbon cloth was cleaned by acetone and distilled water.

Electrocodeposition of nickel oxide and PANI was conducted in a solution containing 0.2M NiSO₄, 5 mM aniline and 0.1M Na₂SO₄ as supporting electrolyte at pH 7.30 by 50 consecutive cyclic voltammetric scans in potential range of -0.3–1.2 V versus SCE at 50 mV s⁻¹. Electrodeposition of nickel oxide or PANI was conducted similarly.

Electroactivities of the films were studied by potential cycling at 5 mV s⁻¹ in 1M NaOH.

Film characterizations

XRD measurements were performed using a Philips PW1710 BASED diffractometer, operated with a Cu K_α radiation source. A Spectrum One FTIR spectropho-

tometer was used to obtain FTIR spectrum of NiO_x/PANI (KBr pellet).

Electrocatalytic properties study

Electrocatalytic properties of NiO_x/PANI composite film were studied by electrooxidations of glucose and fructose in solutions containing 1M NaOH through cyclic voltammetric scans between 0 and 0.6 V at 5 mV s⁻¹.

RESULTS AND DISCUSSION

Electrochemical synthesis and characterizations of NiO_x/PANI

Cyclic voltammetric scans in potential range of ca. 0–1.2 V and ca. -0.3–1.0 V versus SCE are useful methods for electrodeposition of nickel oxide and PANI, respectively.^{8,9} So, electrocodeposition of nickel oxide and PANI is conducted through cyclic voltammetric scans between -0.3 and 1.2 V in the solution containing 0.2M NiSO₄, 5 mM aniline and 0.1M Na₂SO₄ at pH 7.30. After 50 consecutive cyclic scans, the composite film obtained is rinsed with distilled water and then potentially cycled in 1M NaOH. The typical cyclic voltammogram (CV) is in Figure 1 (solid line) together with that of nickel oxide obtained similarly (dash line). Similar to reported NiO_x,^{5,7,9} both the films display a redox pair of Ni(II)/Ni(III) couple on the CVs. However, the current densities on the CV of the composite film are smaller than those on the CV of NiO_x made similarly, indicating that less nickel oxide is present in the composite film. This may be due to the competition of the depositions of nickel oxide and PANI. The releasing of proton during aniline electropolymerization may also depress nickel oxide deposition.¹⁰

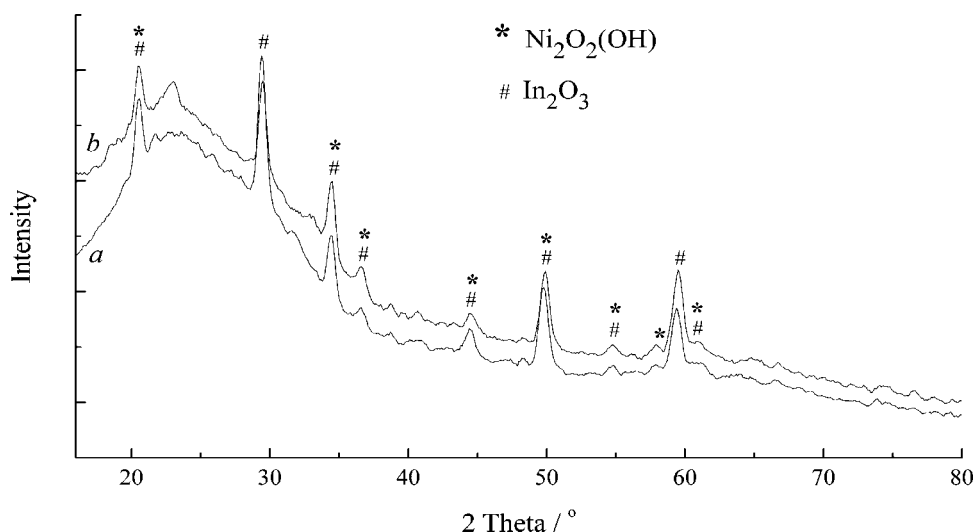


Figure 2 XRD patterns of NiO_x/PANI (a) and NiO_x (b).

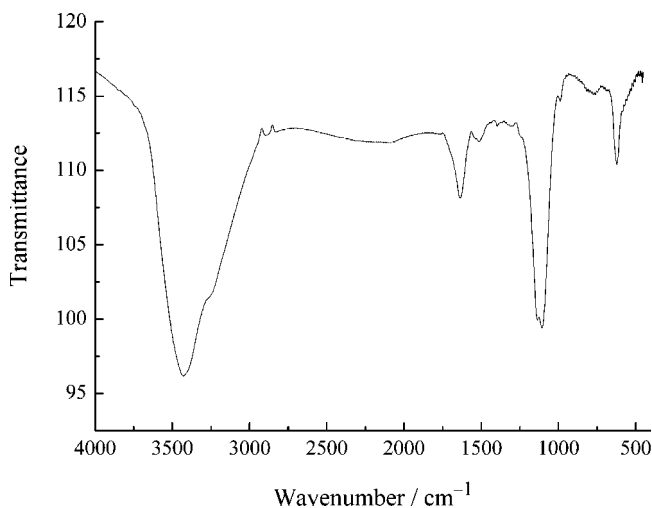


Figure 3 FTIR spectrum of NiO_x/PANI composite film.

To determine the composition of the films, XRD measurements are conducted on the films electrodeposited on ITO glass under similar conditions. Figure 2 shows the XRD patterns of NiO_x/PANI (a) and NiO_x (b). On the basis of the powder diffraction index card No. 00-84-1459, NiO_x exists in the form of Ni₂O₂(OH), which can also be obtained by adding NiSO₄ to excess NaOH solution containing Na₂S₂O₈.¹¹ There are also signals for In₂O₃ (index card No. 00-071-2195) that are due to ITO glass.¹²

The FTIR spectrum of the NiO_x/PANI composite film is shown in Figure 3. The absorptions at 1630 and 1511 cm⁻¹ are due to nitrogen quinonid and benzoid rings. While the absorption of protonated PANI appears at 1132 cm⁻¹, indicating that PANI is protonated in this medium.^{10,13} The peak at 624 cm⁻¹ can be assigned to —O—H group in hydrated nickel oxide.¹⁴

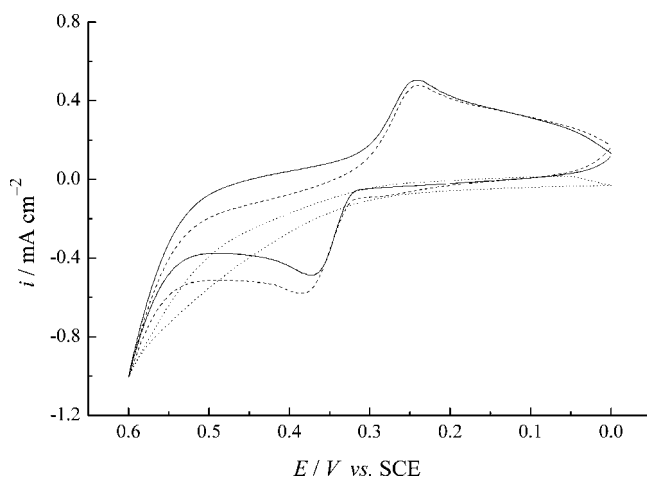


Figure 4 Cyclic voltammograms of NiO_x/PANI composite film (dash line) and carbon cloth electrode (dot line) in 1M NaOH containing 10 mM glucose together with that of the composite film in the absence of glucose (solid line); scan rate: 5 mV s⁻¹.

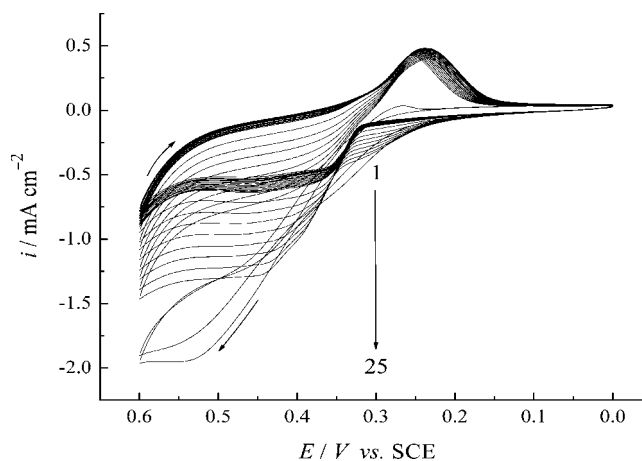


Figure 5 Cyclic voltammograms of NiO_x/PANI in 1M NaOH containing glucose from 0.2 to 300 mM (see text); scan rate: 5 mV s⁻¹.

Electrooxidations of polyhydroxyl compounds on NiO_x/PANI composite film

Electrooxidations of glucose and fructose are conducted on NiO_x/PANI composite film to study its catalytic properties towards electrooxidations of polyhydroxyl compounds.

Figure 4 shows the CV of NiO_x/PANI composite film in 1M NaOH (solid line) together with that in the presence of 10 mM glucose (dash line). The anodic current density increases while the cathodic current density decreases with the addition of glucose. Dotted lines in Figure 4 are the CV of 10 mM glucose on carbon cloth. The absence of any appreciable current indicates that glucose is not effectively electrooxidized on carbon cloth in the explored potential window. Thus, it is clear that glucose is catalytically electrooxidized on NiO_x/PANI composite film. A similar catalytic response is also noted for electrooxidation of fructose.

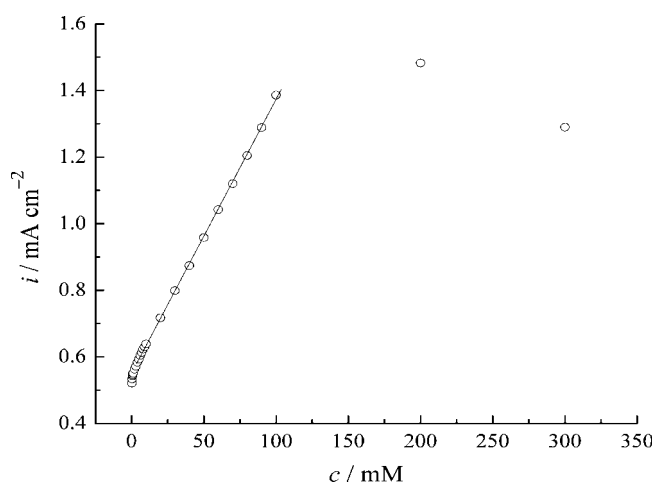


Figure 6 Anodic current densities i_a in Figure 5 at 0.46 V as a function of the concentration of glucose c .

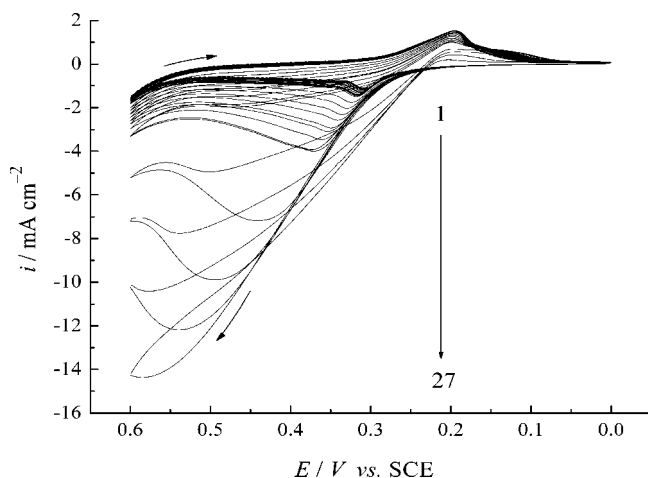
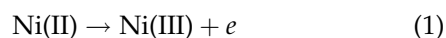


Figure 7 Cyclic voltammograms of NiO_x in 1M NaOH containing glucose from 0.02 to 50 mM (see text); scan rate: 5 mV s⁻¹.

The increase of the anodic current density and the decrease of the cathodic current density upon addition of the polyhydroxy compounds, together with the fact that the organic species are oxidized at the potential where higher oxidation state nickel oxide is produced, which indicate that the compound is oxidized through the mechanism listed below:^{5,15}



Potential application of NiO_x/PANI composite film in analyses of polyhydroxyl compounds

Figure 5 shows the CV of NiO_x/PANI composite film in 1M NaOH solution in the presence of glucose from 0.2 to 300 mM (concentrations of glucose: curves 1 to 5, 0.2 to 1 mM with 0.2 mM step; curves 6 to 14, 2 to 10 mM with 1 mM step; curves 15 to 23, 20 to 100 mM with 10 mM step; curve 24 to 27, 20 to 50 mM with 10 mM step). However, anodic

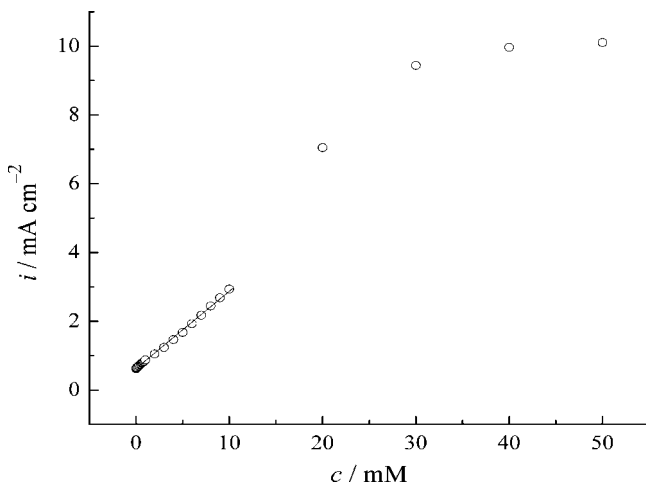


Figure 8 Anodic current densities i_a in Figure 7 at 0.46 V as a function of the concentration of glucose c .

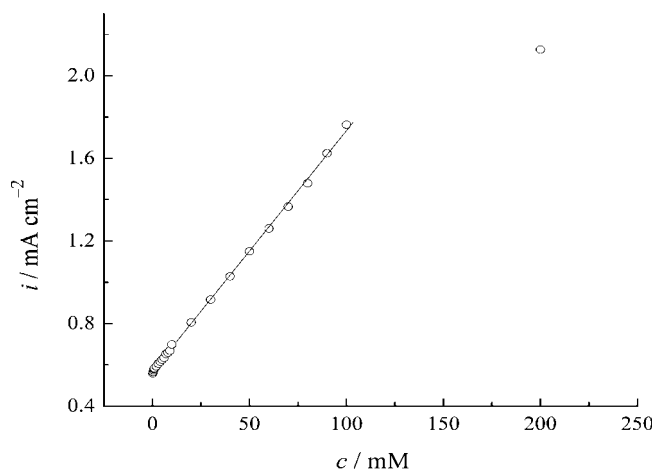


Figure 9 Anodic current densities i_a at 0.46 V on CVs of NiO_x/PANI composite film in 1M NaOH containing fructose from 0.2 to 200 mM as a function of the concentration of fructose c .

with 10 mM step; curve 24, 200 mM; curve 25, 300 mM). The anodic current density i_a at 0.46 V in Figure 5 is linearly dependant on the concentration of glucose c from 1 to 100 mM with $i_a = 0.00822 c + 0.55079$ (coefficient $R = 0.99981$) (Fig. 6). When too much glucose is added into the solution (200 mM or more, curves 24 and 25 in Fig. 5), anodic current residues appear on the negative scans, indicating that the concentration of the polyhydroxyl compound is still high near the electrode even after electrooxidation in the positive scans.

The i_a on the CV of NiO_x also increases when glucose is added into the solution (Fig. 7, concentrations of glucose: curves 1 to 5, 0.02 to 0.1 mM with 0.02 mM step; curves 6 to 14, 0.2 to 1 mM with 0.1 mM step; curves 15 to 23, 2 to 10 mM with 1 mM step; curve 24 to 27, 20 to 50 mM with 10 mM step). However, anodic

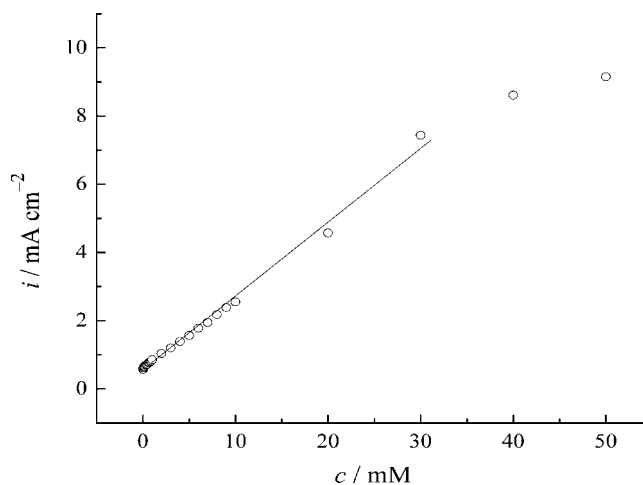


Figure 10 Anodic current densities i_a at 0.46 V on CVs of NiO_x in 1M NaOH containing fructose from 0.02 to 50 mM as a function of the concentration of fructose c .

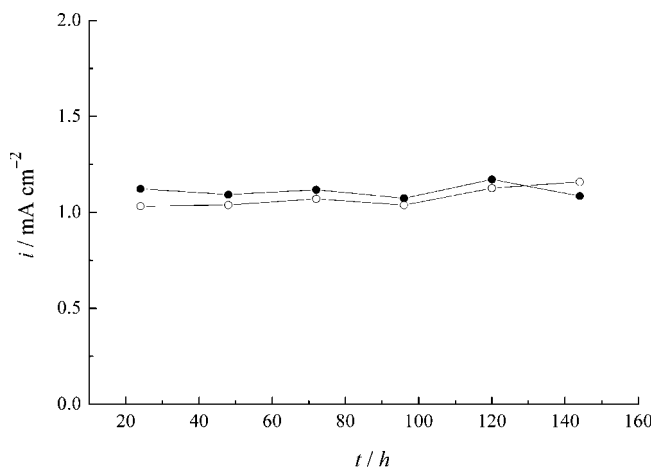


Figure 11 The stability of NiO_x/PANI composite film for measurement of 10 mM glucose (circle) and 10 mM fructose (dot).

current residues appear on the negative scans when the glucose concentration is only more than 10 mM, and so the linear range of i_a versus c for glucose oxidation is limited to 0.1 to 10 mM (Fig. 8: $i_a = 0.22461c + 0.62502$, $R = 0.99885$). This is because when the concentration of glucose is very high, the catalyst could no longer cope. The higher linear limit for glucose electrooxidation on the composite film than on NiO_x indicates that the catalytic efficiency is raised upon composite formation.

Electrooxidation of fructose on either NiO_x/PANI or NiO_x shows similar CV to that of glucose. The i_a is linearly dependent on fructose concentration from 10 to 100 mM on NiO_x/PANI (Fig. 9: $i_a = 0.01166c + 0.5697$, $R = 0.99911$) and 0.1 to 30 mM on NiO_x (Fig. 10: $i_a = 0.21624c + 0.56375$, $R = 0.99638$).

The polymer network in NiO_x/PANI composite may provide 3D system for the catalytic particles and so the composite displays high efficiency for the catalytic reaction. So the range of the linear dependence of i_a versus c is enlarged for the electrooxidations of polyhydroxyl compounds after composite formation.

The storage and operational stability of the composite film is in Figure 11. It could be seen that the change of the response for glucose and fructose is less than 5% and 12.9%, respectively, after 1 week.

CONCLUSIONS

NiO_x/PANI composite film was obtained through cyclic voltammetric scans in the solution containing

NiSO₄ and aniline at pH = 7.30. Ni₂O₂(OH) was detected through XRD measurements for both the composite film and similarly prepared NiO_x. Characteristic absorptions of PANI appeared on the FTIR spectrum of the composite film together with the absorption of —O—H group in hydrated nickel oxide. The presence of the vibrational band at 1132 cm⁻¹ indicated that PANI was protonated in this media, which may be due to proton releasing during aniline polymerization. The cyclic voltammogram (CV) of the composite film displayed well-defined anodic and cathodic peaks associated with Ni(II)/Ni(III) redox couple. Catalytic electrooxidations of glucose and fructose occurred positively than this redox couple, suggesting that the electron transfer was mediated involving nickel oxidation. The anodic current density i_a at 0.46 V exhibited a linear dependence on the concentration c of the polyhydroxyl compound in a comparatively larger range from 1 to 100 mM for glucose (0.1 to 10 mM on NiO_x) and 10 to 100 mM for fructose (0.1 to 30 mM on NiO_x), respectively. The change of the response of the composite film for glucose and fructose is less than 5% and 12.9%, respectively, after 1 week. This provided the composite film potential applications in analytical procedures for determining polyhydroxyl compounds.

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