

Methanol, Ethanol, and Glycerol Oxidation by Graphite-Epoxy Composite Electrodes with Graphene-Anchored Nickel Oxyhydroxide Nanoparticles [†]

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Abstract: In this work, a graphite-epoxy electrode with cyclic voltammetry electrodeposited reduced graphene oxide and nickel oxyhydroxide nanoparticles was prepared by decomposition in NaOH alkaline solution of cyclic voltammetry electrodeposited nickel hexacyanoferrate. FE-SEM studies were performed to confirm the NiOOH nanoparticle; the average size of the NiOOH nanoparticles was 61 ± 16 nm and EDX was applied to analyze chemical composition. To verify the performance of the prepared electrode, it was used in the electrooxidation of alcohols in alkaline medium by cyclic voltammetry. By performing different calibration experiments of methanol, ethanol, and glycerol, it was possible to extract some information about the electrode in the presence of alcohols. The LOD for methanol, ethanol, and glycerol were 2.16 mM, 2.73 mM and 0.09 mM, respectively, with sensitivity values of $1.32 \mu\text{A mM}^{-1}$, $1.80 \mu\text{A mM}^{-1}$ and $24.60 \mu\text{A mM}^{-1}$, respectively. Multivariate inspection of the data using Principal Component Analysis (performed with the ClustVis online tool) demonstrated the potential ability to discriminate between the different alcohols, whereas the explained variance with the first two components was as high as 89.7%.

Keywords: composite electrode; glycerol; ethanol; methanol; electro-oxidation

1. Introduction

Composite materials have garnered interest in many areas of knowledge [1]. It consists of joining various materials in order to form another material that offers better properties [2]. Carbon-based composite materials have shown great advances in science and can be used in conjunction with graphene oxide (GO) and metal nanoparticle catalysts for applications in supercapacitors [3], fuel cell electrocatalysts [4], and sensors [5] among others.

According to Zhu and colleagues [6], graphene oxide can be considered an excellent material due to its mechanical and electrical properties. Moreover, its high tolerance to chemical change is beneficial because it provides controlled chemical environments for active metal species due to their functional groups (COOH, OH and O), which are reactive species that aid in the heterogeneous nucleation of metal nanoparticles [7].

LI, Su-Juan et al. [8] synthesized NiOOH nanosheets using a hydrothermal method to study the oxidation of glucose and methanol. It was reported that NiOOH nanosheets provided remarkable catalytic activity and improved stability for the oxidation of glucose and methanol due to their structural properties such as high contact surface and a more homogeneous distribution of surface nanostructures.

Thus, graphene oxide combined with nickel oxyhydroxide on carbon surface could be an interesting alternative way to obtain nanomaterials, such as electrocatalysts [8]. Thus, the present work sought to obtain the electrosynthesis of a composite material through a simple methodology, based on graphene oxide and nickel oxyhydroxide on graphite/epoxy support through the cyclic voltammetry technique, aiming at the potentiality of this composite in devices such as electrochemical sensors and electrocatalysts in fuel cells.

2. Materials and Methods

2.1. Preparation of Graphite/Epoxy Electrodes

The electrodes were assembled using a PVC tube body. A small copper disk was welded at the electrical connector [9]. After the electrodes (EG) were assembled, a composite graphite-epoxy mixture was prepared by manually mixing the epoxy resin, the hardener, and the graphite powder. The resulting slurry was homogenized by mixing for 45 min, then cured at 40 °C for 2 days [10]. The electrodes were then washed with MilliQ water (Millipore, Billerica, MA, USA) and sanded using 300, 600, 800, and blue luster sandpaper 1200, respectively, until the acquisition of a clear and homogeneous surface.

2.2. Electrosynthesis of Nickel Oxyhydroxide Nanoparticles on Reduced Graphene Oxide

The formation of the nickel oxyhydroxide sensor with graphene oxide was done in three steps, in a similar way as in the literature [11]; the solution was prepared using 1.0 mg mL⁻¹ of graphene oxide (GO) from a solution of 5.0 mg mL⁻¹ of GO, where there was a dilution process in 0.067 mol L⁻¹ phosphate buffer. Thus, electrodeposition of the graphene oxide occurred by cyclic voltammetry for 10 consecutive sweeps in a range of -1.5 V to 0.5 V with a scanning speed of 10 mV s⁻¹ in GO dispersion with magnetic stirring. After deposition, the electrodes were tested in 5 mmol L⁻¹ K₃Fe(CN)₆ solution in 1.0 mol L⁻¹ KCl in a range of -0.2 V to 0.8 V at a scanning speed of 50 mV s⁻¹.

After deposition of rGO, the deposition of NiHCF films was analogous to the literature [5]. They were electrodeposited by cyclic voltammetry for 15 potential cycles between -0.2 V and 1.0 V using a scan rate of 100 mV s⁻¹ in a solution of 0.5 mol L⁻¹ of KCl composed of 0.1 mol L⁻¹ of HCl, 0.5 mmol L⁻¹ of K₃Fe(CN)₆, and 1.0 mmol L⁻¹ of Ni(NO₃)₂.

Subsequently, the formation of nickel oxyhydroxide nanoparticles on the electrode surface was performed by cyclic voltammetry during 36 consecutive potential sweeps of -0.5 V at 1.0 V at 100 mV s⁻¹ in a solution of 0.5 mol L⁻¹ of sodium hydroxide (NaOH). Finally, the electrodes were cycled in 0.10 mol L⁻¹ NaOH solution under a potential of -1.0 V at 1.0 V and 100 mV s⁻¹ for surface passivation.

2.3. Characterization by Scanning Electron Microscopy

The spectroscopic characterizations of the modified composites electrodes were carried out in a graphite/epoxy electrode (EGC) with area covering 1.13 cm². Scanning Electron Microscopy (SEM) modified the morphological characterization of the GC surface. A scanning electron microscope with field emission gun (FEG-SEM) from Zeiss (model MERLIN SM0087) and energy dispersive X-ray spectroscopy (EDX) module model from Oxford Instruments, X-MAX (20mm²), was used for the measurements.

2.4. Measuring Procedure

The amperometric measurement cell was formed by the four-metal modified electrodes plus a Fisherbrand ORP reference Ag/AgCl electrode (Fisher Scientific, Madrid, Spain). Cyclic voltammetry

measurements were taken using a 6-channel AUTOLAB PGSTAT20 potentiostat (Ecochemie, Utrecht, The Netherlands) in multichannel configuration using the GPES Multichannel 4.7 software package. For this, potentials were cycled between -1.0 V and $+1.0$ V vs. Ag/AgCl, with a scan rate of 100 mV s $^{-1}$. All electroanalytical experiments were performed at room temperature (25 °C). The obtained responses were analyzed by means of the different chemometric tools described below.

For the study of main components (PCA), we used an open web tool called Clustvis (<https://biit.cs.ut.ee/clustvis/>) that visualizes clusters of multivariate data. It uses several R packages internally, including brilliant, ggplot2, pheatmap, gridSVG, RColorBrewer, FactoMineR, pcaMethods, gProfileR, shinyBS, and shinyjs, among others [12].

3. Results and Discussion

3.1. Characterization of Composite Electrode EG/rGO/np-NiOOH

The successful electrosynthesis of nickel oxyhydroxide nanoparticles on reduced graphene oxide was confirmed by FEG-SEM and EDX. Figure 1A shows that the EG/rGO/np-NiOOH nanoparticles have a homogeneous distribution on the surface of the electrode. NiOOH nanoparticles have an average size of 61 ± 16 nm (Figure 1B) and are in the form of small balls. In Figure 2, it is possible to observe the EDX spectrum of the EG/rGO/np-NiOOH electrode. The EDX shows that the surface is composed of Ni, O, and C, indicating that the electrosynthesis of nickel oxyhydroxide from nickel hexacyanoferrate (NiHCF) was a success, not presenting the elements Fe and K in the spectrum.

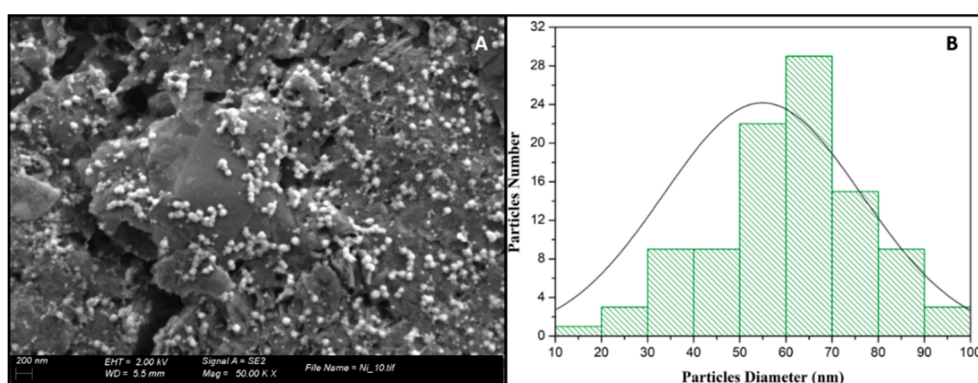


Figure 1. (A) FEG-SEM images for the EG/rGO/np-NiOOH electrode; (B) histogram of nanoparticles in the EG/rGO/np-NiOOH electrode.

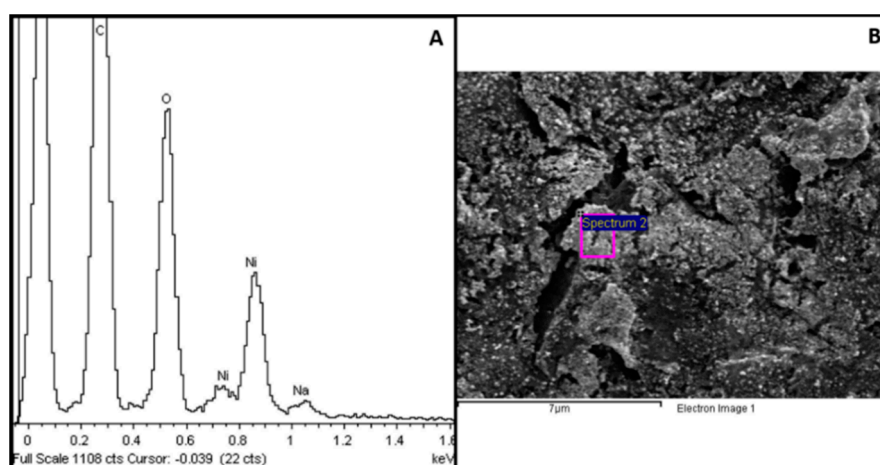


Figure 2. (A) EDX spectrum of the EG/rGO/np-NiOOH electrode (1.6 keV); (B) FEG-SEM images with EDX spectrum of the EG/rGO/np-NiOOH electrode.

3.2. Electrochemical Behaviour of Alcohols on the EG/rGO/np-NiOOH Modified Electrode

The electrooxidation of alcohols on the electrode EG/GO/np-NiOOH, as observed in Figure 3A, at a potential near 0.65 V vs. Ag/AgCl related to the increase of the anodic peak current and increase of the cathodic peak current. The results suggest that Ni(III)/Ni(II) redox can catalyze an electrooxidation of alcohols [13–15]. According to [16,17], main component analysis (PCA) is a set of mathematical algorithms capable of reducing the dimensionality of the data, retaining the main and most part of the variation in the data set. It is possible to perform a reduction that identifies directions, the so-called main components, along which the variation in the data is maximum, usually plotted in 2D or 3D. This plot depends on the amount (%PC) accumulated in the dimensions, an amount of 70% in PC1 + PC2 may be enough to plot the data in 2D and be able to analyze completely; however, when there are smaller values, PC3 is required and a 3D graph is generated to carry out the analyses. By using some components, each sample can be represented by relatively smaller numbers, rather than thousands of variables [18]. In Figure 3B, the PCA is shown for the EG/rGO/np-NiOOH modified electrodes. The PCA was prepared by treating the sensitivities of the sensor for alcohols. It was observed that for the sensors studied, an 89.7% accumulation of variance was explained in the first two PCs, meaning that all the original information is contained in these two coordinates. Another point to note is that glycerol differs greatly from ethanol and methanol; however, ethanol and methanol may be somewhat similar. We can attribute the equality of ethanol and methanol to the immense similarity between their chains, where the ethanol comes after methanol; the two compounds presented many similarities in the analyses. Multivariate inspection of the data using Principal Component Analysis (performed with use of the ClustVis online tool) demonstrated the potential ability to discriminate between the different alcohols, whereas the explained variance with the first two components was as high as 89.7%.

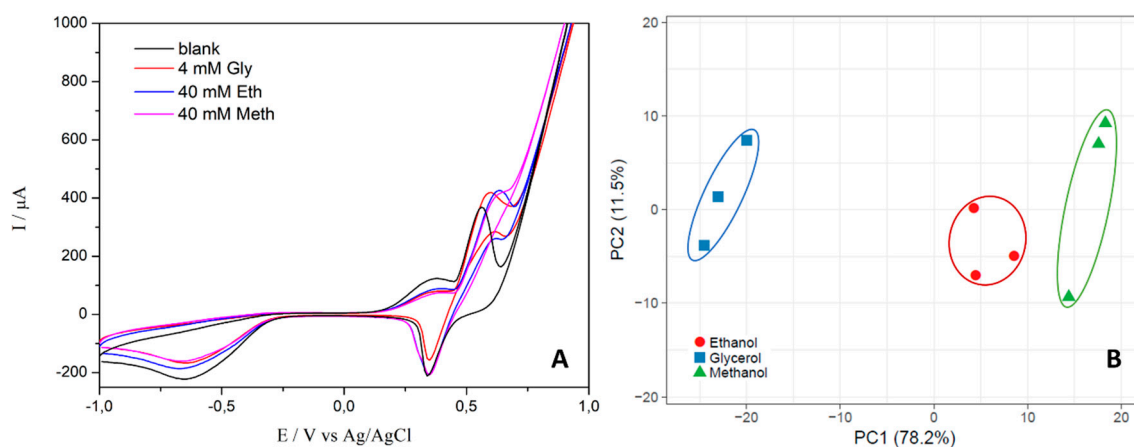


Figure 3. (A) Cyclic voltammograms obtained with EG/GO/np-NiOOH modified electrode for alcohol solutions $4.0 \times 10^{-3} \text{ mol L}^{-1}$ of glycerol and $40.0 \times 10^{-3} \text{ mol L}^{-1}$ of ethanol and methanol in 0.10 mol L^{-1} NaOH. (Blank) = Absence, (Gly) = Glycerol, (Eth) = Ethanol and (Meth) = Methanol presence; (B) Score plot of the first two components obtained after PCA quadruplicate analysis of different amounts of glycerol, ethanol, and methanol.

The analytical stability (%RSD) of the sensor was estimated using mixed solutions of $5.0 \times 10^{-3} \text{ mol L}^{-1}$ glycerol and $50.0 \times 10^{-3} \text{ mol L}^{-1}$ ethanol and methanol over 27 measurements; for EG/rGO/np-NiOOH, a value of 5.02% was obtained. Full calibrations of considered alcohols were conducted in 0.10 mol L^{-1} NaOH solution with a scan rate of 100 mV s^{-1} , for the complete characterization of the sensor used. Table 1 shows the electrochemical parameters for all the alcohols studied. We observed that the modified electrode EG/rGO/np-NiOOH for glycerol has good amperometric sensitivity, but for ethanol and methanol, they are smaller. The values of the limit of detection and quantification are reasonably close, which means that the behavior of the different alcohols in the electrode is comparable. Therefore, we can apply the modified electrode in the same concentration range for all alcohols considered.

Table 1. Analytical parameters for various alcohols using the EG/rGO/np-NiOOH modified electrode in 0.10 mol L⁻¹ NaOH by Cyclic Voltammetry ($v = 100 \text{ mV s}^{-1}$; $n = 4$).

Alcohol	Limit of Detection (mM)	Limit of Quantification (mM)	Sensitivity ($\mu\text{A mM}^{-1}$)	Concentration Range (mM)
Glycerol	0.09	0.31	24.60	1.0–4.0
Ethanol	2.73	9.11	1.80	10.0–40.0
Methanol	2.16	7.19	1.32	10.0–40.0

4. Conclusions

In summary, a novel EG/rGO/np-NiOOH nanocomposites were prepared in three steps by the electrodeposition method. EDX confirmed the success of electrosynthesis of nickel oxyhydroxide in reduced graphene oxide. FEG-SEM characterization showed the NiOOH nanoparticles with an average size of $61 \pm 16 \text{ nm}$ decorated on the EG/rGO sheets. The as-synthesized EG/rGO/NiOOH nanocomposites exhibit excellent electrochemical behavior towards the oxidation of glycerol, ethanol, and methanol. The proposed alcohols sensor showed the LOD for methanol, ethanol and glycerol as 2.16 mM, 2.73 mM, and 0.09 mM, respectively, with sensitivity values of $1.32 \mu\text{A mM}^{-1}$, $1.80 \mu\text{A mM}^{-1}$ and $24.60 \mu\text{A mM}^{-1}$. Multivariate inspection of the data using Principal Component Analysis (performed with use of the ClustVis online tool) demonstrated the potential ability to discriminate between the different alcohols, whereas the explained variance with the first two components was as high as 89.7%.

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Conflicts of Interest: The authors declare no conflict of interest.

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