

Chapter 43

Electro-Oxidation of Formic Acid, Glucose, and Methanol at Nickel Oxide Nanoparticle Modified Platinum Electrodes

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Abstract The current study presents a comparison for the electro-oxidation of formic acid (FA), glucose (GL), and methanol (ME) at nickel oxide nanoparticles (NiOx) modified electrodes. The modification with NiOx was pursued onto a bare glassy carbon (GC) and Pt-modified (Pt/GC) electrodes electrochemically, and the catalytic activity was measured in 0.3 M NaOH. Cyclic voltammetry (CV), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) are all used to provide a concrete characterization of the prepared electrodes. A catalytic enhancement of GL oxidation (GLO) and ME oxidation (MEO) was observed at the NiOx-modified GC (NiOx/GC) electrode, while the same electrode did not show any activity towards FA oxidation (FAO), revealing that FAO is substrate dependent. On the other hand, assembling NiOx onto the Pt/GC electrode assisted in improving the catalytic activity of all reactions (GLO, MEO, and FAO). The catalytic enhancement observed at the NiOx/Pt/GC electrode for GLO, MEO, and FAO was not only confined in the large increase of the oxidation current but also in a negative shift in the onset potential of the oxidation reaction. We believe NiOx could successfully play an essential role in this catalytic enhancement, presumably via participation in these reactions in a way facilitating the charge transfer or providing the oxygen atmosphere necessary for promoting an oxidative removal for unwanted poisoning species.

Keywords Electrocatalysis • Nickel oxide nanoparticles • Platinum nanoparticles • Fuel cells

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43.1 Introduction

Fuel cells (FCs) are systems for conversion of energy on a continuous regime. The smallest and easiest fuel for these devices is hydrogen. However, the use of hydrogen presents some significant drawbacks related to its explosive and flammable nature, which makes its storage and transportation problematic [1]. Therefore, different other small organic molecules have been proposed as fuels to substitute hydrogen. Among these fuels, formic acid (FA), glucose (GL), and methanol (ME) have been shown interesting oxidation efficiency. Actually, these organic molecules are commercially available and environmentally safe, which invokes no problem in transportation and storage [2–4].

Typically, these fuels are injected to the anodic part of FCs and oxidized at certain anodic catalysts of reasonable catalytic activity. Platinum represents the most widely used anodic catalyst for these anodic processes, particularly in the low temperature regime [5, 6]. However, the generation of strongly adsorbed poisoning intermediates (e.g., CO_{ad} and other carbonaceous materials), which are generally produced during the oxidation process, can ultimately hinder the oxidation process and deteriorate the catalytic activity of the catalyst, which ultimately leads to a severe failure of FCs as a whole [7].

Recently, Pt–M-based binary catalysts, where M = Ru, Ir, Mo, Os, or Ni are recommended to enhance the catalytic activity towards the oxidation of these fuels by eliminating or inhibiting the CO poisoning effect [3, 4, 8–10]. Effort is expanded to develop new ternary or quaternary alloy catalysts for these oxidation processes [11].

This study compares the catalytic activity of a new catalyst developed by electrodepositing crystallographically oriented nickel oxide nanoparticles (NiOx) on Pt surfaces [12] towards FA oxidation (FAO), GL oxidation (GLO), and ME oxidation (MEO) in alkaline media. NiOx is believed to provide the oxygen species to the adsorbed poisoning intermediates to enhance their oxidative removal at low potential.

43.2 Experimental

The working electrode was a glassy carbon (GC) rod ($d = 3.0$ mm) sealed in a Teflon jacket leaving an exposed geometric surface area of 0.07 cm². A spiral Pt wire and an Ag/AgCl/KCl (sat.) were used as the counter and the reference electrodes, respectively. Conventional methods were applied for cleaning the working electrode [3]. Platinum nanoparticles (PtNPs) were electrodeposited on GC (next noted as Pt/GC) electrodes from an acidic solution of 0.1 M H_2SO_4 containing 2.0 mM H_2PtCl_6 using potential step electrolysis from 1 to 0.1 V vs. Ag/AgCl/KCl (sat.) for 500 s. This resulted in the deposition of 4.3 μg of Pt (as estimated from the charge of the i - t curve recorded during the potentiostatic

electrolysis). On the other hand, the modification of the GC and Pt/GC electrodes with NiOx (next noted as NiOx/GC and NiOx/Pt/GC, respectively) was achieved in two steps. First, Ni was electrodeposited from an aqueous 0.1 M acetate buffer solution (ABS, pH = 4.0) containing 1 mM Ni(NO₃)₂ by constant potential electrolysis at -1 V vs. Ag/AgCl/KCl (sat.) for 120 s. Next, an electrochemical passivation step for Ni was carried out in 0.1 M phosphate buffer solution (PBS, pH = 7) to allow the formation of NiOx [3, 12].

Cyclic voltammetric (CV) measurements were performed in a conventional two-compartment three-electrode glass cell. All measurements were performed at room temperature (25 ± 1 °C) using an EG&G potentiostat (model 273A) operated with Echem 270 software. A field emission scanning electron microscope (FE-SEM, QUANTA FEG 250) coupled with an energy dispersive X-ray spectrometer (EDS) unit was employed to evaluate the electrode's morphology. The electrocatalytic activity of the NiOx/GC and NiOx/Pt/GC electrodes towards FAO, GLO, and MEO was examined in a solution of 0.3 M NaOH containing 0.3 M FA, 40 mM glucose, and 0.3 M methanol, respectively. All chemicals were used without further purification. Current densities were calculated on the basis of the real surface area. The surface coverage θ of NiOx on the Pt/GC electrode was estimated from the decrease of the peak current intensity at ca. 0.4 V corresponding to the reduction of the Pt surface oxide formed during the anodic scan [13, 14] (see later Fig. 43.2d).

43.3 Results and Discussion

43.3.1 Materials and Electrochemical characterization

The morphological characterization of the modified electrodes was disclosed by FE-SEM imaging. Figure 43.1a shows the typical FE-SEM micrograph of NiOx/GC electrode after regular passivation (the inset depicts the morphology of the same electrode before passivation). It looks the electrodeposition of metallic Ni has occurred in a dendritic nanostructure with an average particle size of 80 nm that partially covers the surface of the GC electrode. After the electrochemical passivation, the average particle size of NiOx increased to ca. 120 nm, which infers the aggregation of Ni particles during the passivation. Figure 43.1b, showing the SEM micrograph for Pt/GC electrode, depicts round-shape Pt nanoparticles with reasonably uniform size and density distribution and a particle size of ca. 100 nm. At the NiOx/Pt/GC electrode (Fig. 43.1c), a flower-like Pt and Ni nanostructures are obtained with a significantly larger average particle size compared with Fig. 43.1a, b. The EDX spectrum for the NiOx/Pt/GC electrode was disclosed in Fig. 43.1d. It indicates that both Pt and Ni coexist at the surface of the modified GC electrode, which is helpful in understanding the catalytic activity and poisoning.

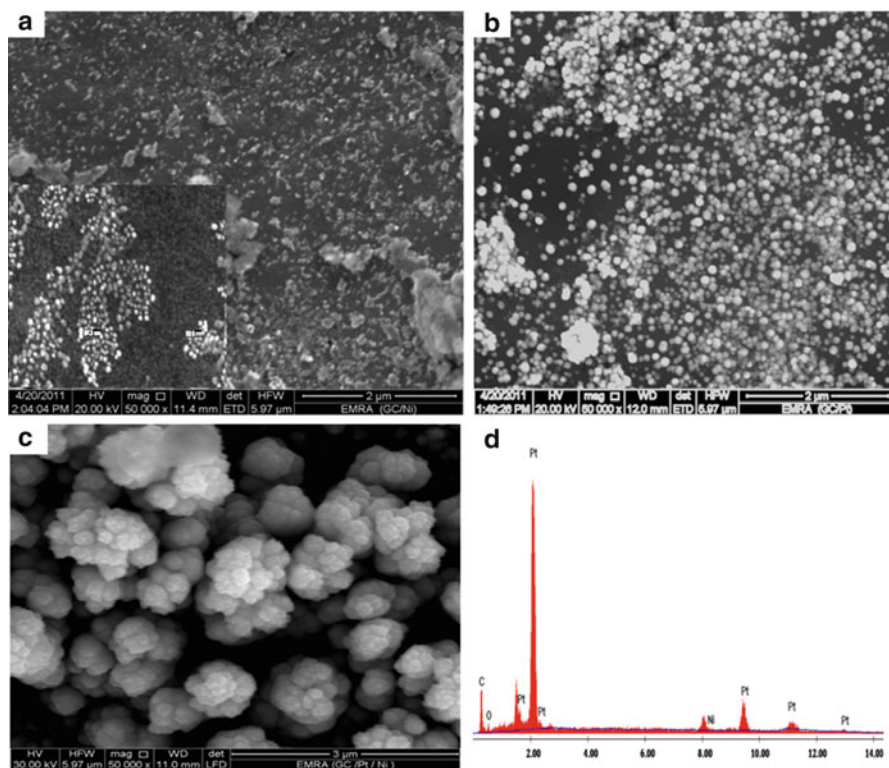


Fig. 43.1 FE-SEM micrographs obtained for NiOx/GC (*inset*, Ni/GC) (a), Pt/GC (b), NiOx/Pt/GC (c). EDX chart for the NiOx/Pt/GC (d)

Figure 43.2a–d shows CVs for GC (a), NiOx/GC (b), Pt/GC (c), NiOx/Pt/GC (d) electrodes, respectively, in 0.3 M NaOH at a scan rate of 200 mV s^{-1} . Figure 43.2a depicts the absence of any electrochemical response at the bare GC electrode under the operating conditions of potential and pH. While, at the NiOx/GC electrode (Figure 43.2b), a well-defined redox waves appeared around 0.4 V vs. Ag/AgCl/KCl(sat.) corresponding to a surface confined Ni(II)/Ni(III) reversible transformation, which stands as a characteristic feature for NiOx deposition [12, 15]. At the Pt/GC electrode (Fig. 43.2c), the characteristic response of polycrystalline Pt surface is obtained, inferring the successful deposition of PtNPs. Typically, a broad oxidation peak for the Pt oxide in the potential range of ca. -100 to 600 mV vs. Ag/AgCl/KCl (sat.) coupled with a single reduction peak centered at ca. -0.3 V vs. Ag/AgCl/KCl appeared. In addition, well-defined peaks of the hydrogen adsorption–desorption ($H_{\text{ads/des}}$) appeared at potential negative to -0.5 V vs. Ag/AgCl/KCl [3].

Interestingly, the modification of the Pt/GC electrode with NiOx (Fig. 43.2d) resulted in a noticeable decrease in the intensity of the Pt oxide reduction peak (at ca. -0.34 V) along with a decrease in the current intensity of the ($H_{\text{ads/des}}$) peaks

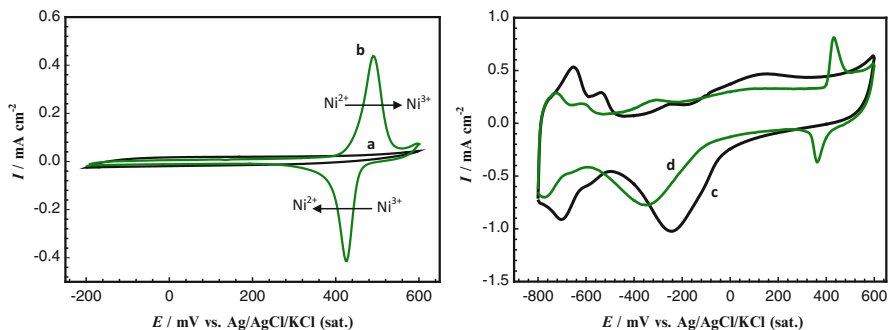


Fig. 43.2 CVs of GC (a), NiOx/GC (b), Pt/GC (c), and NiOx/Pt/GC (d) electrodes in 0.5 M NaOH solution at a scan rate 200 mV s^{-1}

(in the potential region from -0.6 to $-0.9 \text{ V vs. Ag/AgCl/KCl (sat)}$) and hence, the accessible surface area of Pt is decreased (surface coverage of NiOx $\approx 25 \%$). In addition, a redox pair appears at ca. 0.45 V corresponding to the Ni(II)/Ni(III) reversible transformation [3, 12].

43.3.2 Electrocatalytic activity towards FAO, GLO, and MEO

The electrocatalytic activity of the various modified GC electrodes towards FAO, GLO, and MEO is addressed by measuring CVs in 0.3 M NaOH solution containing a definite concentration of each fuel at a scan rate 200 mV s^{-1} . Figure 43.3 shows the CVs obtained at the GC (a, c, and e) and NiOx/GC (b, d, and f) for FAO, GLO, and MEO, respectively. Basically, there was no electrochemical activity for all fuels at the bare GC electrode within the applied conditions of pH and potential (Fig. 43.3a, c, and e). The NiOx/GC electrode did not show any significant catalytic activity towards FAO, except increasing the charging current due to the presence of NiOx at the GC surface (Fig. 43.3b). This obviously depicts that FAO is a substrate-dependent reaction [16]. On the other hand, the same NiOx/GC electrode exhibited a reasonable catalytic activity towards GLO if compared to the bare GC electrode (Fig. 43.3d). NiOx is believed to act as a catalytic mediator in GLO in such a way facilitating the reaction kinetics [15, 17]. We believe that the adsorbed GL molecules at the surface of the electrode are oxidized at a high potential coincident with the Ni(II)/Ni(III) transformation. This process leads to reduce the number of active sites for glucose adsorption that, along with the poisoning effect of the products or intermediates of the reaction, tends to decrease the overall rate of glucose oxidation. Thus, the anodic current passes through a maximum in the forward scan.

It is worth mentioning that the electrocatalytic GLO occurs not only in the forward scan but also in the backward scan. Interestingly, in the backward scan,

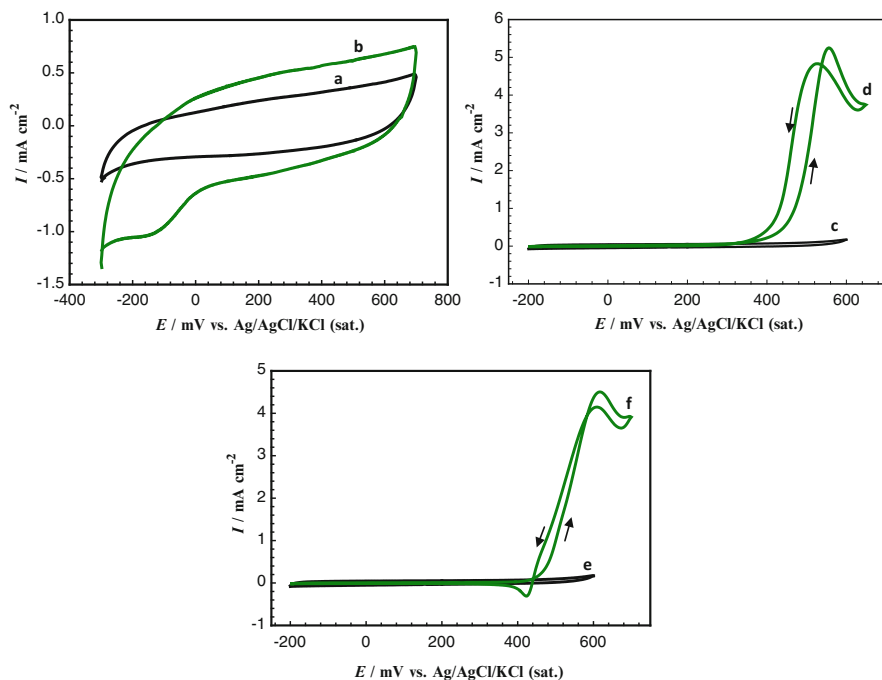


Fig. 43.3 (a–f) CVs for GC (a, c, e), NiOx/GC (b, d, f) electrodes in 0.3 M NaOH containing 0.3 M FA, 40 mM glucose, and 0.3 M methanol oxidation measured at 200 mV s^{-1} , respectively

the oxidation current continues increasing to pass by a maximum due to the regeneration of active sites occupied by poisoning intermediates and product such as gluconolactone [15, 18] to participate again in GLO. Hence, the mechanism of GLO at the NiOx/GC electrode can be described as

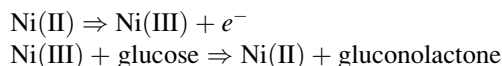


Figure 43.3f shows the electrocatalytic response of NiOx/GC towards methanol oxidation. As has happened for GLO, the electrocatalytic activity towards MOR has increased at the NiOx/GC electrode, in agreement with previous results [17, 19]. The mechanism of MEO at NiOx/GC electrode can be described similarly, presuming that NiOx could act as a catalytic mediator to facilitate the oxidation kinetics. However, a minor reduction peak was observed during the reverse scan of MEO at NiOx/GC, which may be attributed to reduction of remaining NiOOH [19].

Figure 43.4 shows the CVs obtained at Pt/GC (a, c, and e) and NiOx/Pt/GC (b, d, and f) for FAO, GLO, and MEO, respectively, in 0.3 M NaOH solution containing definite concentration for each fuel at 200 mV s^{-1} . Figure 43.4a shows the CVs responses for FAO at Pt/GC electrode, which appeared similar to that observed at bulk polycrystalline Pt substrates. In the forward scan, two oxidation peaks

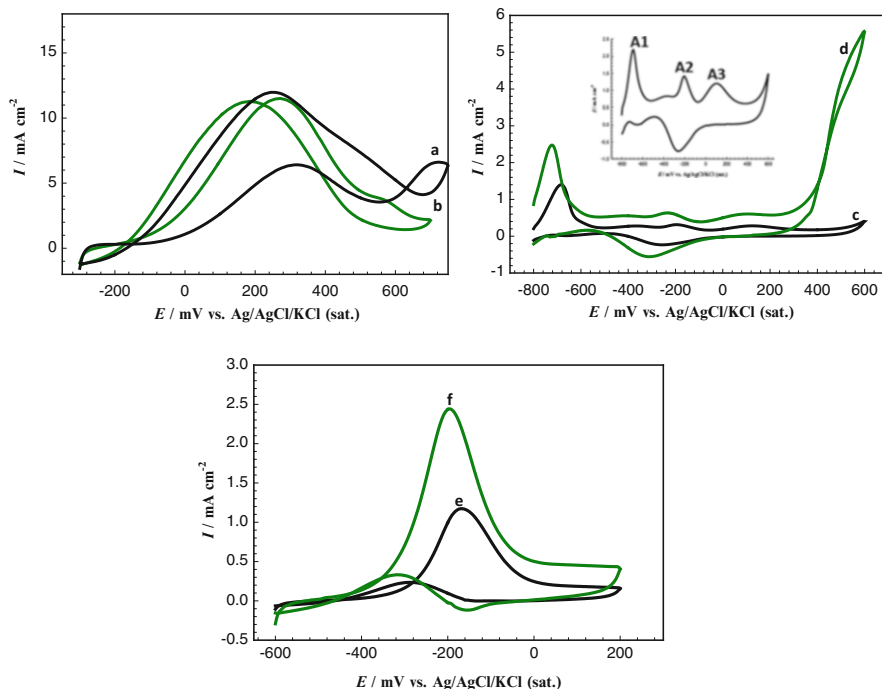


Fig. 43.4 (a–f) CVs for Pt/GC (a, c, e) and NiOx/Pt/GC (b, d, f) electrodes in 0.3 M NaOH containing 0.3 M FA, 40 mM glucose, and 0.3 M methanol oxidation measured at 200 mV s^{-1} , respectively. *Inset*, is the curve c for glucose oxidation at Pt/GC electrode to clear the oxidation process

appeared; the first (I_p^d , at ca. 0.25 V) is assigned to the direct FAO to CO_2 (dehydrogenation pathway), while the second (dehydration pathway (I_p^{ind}), at ca. 0.65 V) to the oxidation of the adsorbed poisoning CO intermediate (produced from non-faradaic dissociation of FA) to CO_2 [16, 20]. Oxidation current is also observed during the backward scan with a higher current (I_b). This is simply because the retrieval of the Pt active sites from the poisoning CO, which is accelerated after being the Pt surface mostly hydroxylated Pt–OH_{ad} [3, 16].

On the other hand, at the NiOx/Pt/GC electrode (Fig. 43.4b), several interesting features appear:

- (I) A significant enhancement of I_p^d with a concurrent depression of I_p^{ind} . This may be attributed to the impact of NiOx in retarding the formation of CO and/or accelerating its oxidative removal at low potential [16, 20].
- (II) The I_p^d/I_b ratio approaches unity in a similar fashion to the ideal catalyst (Pd) for FAO. This indicates that less amount of CO is produced in the forward scan at the NiOx/Pt/GC electrode than at the Pt/GC electrode [3, 21].

The mechanism of FAO at the NiOx/Pt/GC was discussed in detail previously [3, 16].

Figure 43.4c shows the CV responses for glucose oxidation at Pt/GC electrode in 0.3 M NaOH containing 40 mM glucose at a scan rate 200 mV s^{-1} , and the oxidation behavior appears clearly in the inset of this figure. Inspection of this figure (inset) reveals that there are three clear oxidation peaks A1, A2, and A3 for GLO on the forward scan at the Pt/GC electrode in agreement with previous results [2, 22]. The peak A1 is due to the chemisorption and dehydrogenation of GL in the hydrogen region with the removal of the first hydrogen atom (considered the rate determining step). The dehydrogenated intermediate formed by electro-oxidation at A1 leads to formation of gluconate by successive steps. The peak A2 appears at Pt-OH_{ads} adsorbed catalyst surface by direct glucose oxidation from the bulk to lactone (double layer region), which on hydrolysis produces gluconate. The peak A3 is obtained on already oxidized catalyst surface and may be due to oxidation of adsorbed residues [2, 22].

On the other hand, at NiOx/Pt/GC electrode, catalytic activity is enhanced (Fig. 43.4d). That is, the peak A1 appears at a more negative potential than Pt/GC electrode. In addition, the peak current of the peaks (A1, A2, and A3) at NiOx/Pt/GC electrode is substantially higher than that of the Pt/GC electrode. Another peak appears on the case of NiOx/Pt/GC on the potential range higher than 400 mV vs. Ag/AgCl/KCl (sat.). This peak is attributed to GLO at NiOx only (no contribution from Pt) in parallel with the Ni(II)/Ni(III) transformation, as observed at NiOx/GC electrode (Fig. 43.3d). The enhanced electrocatalytic activity for NiOx/Pt/GC electrode towards GLO may be attributed to the role of NiOx in providing the oxygen species necessary for the oxidative removal of poisoning species at lower potential compared to the unmodified Pt electrode.

Figure 43.4e shows the CV responses for methanol oxidation at Pt/GC electrode at a scan rate 200 mV s^{-1} . Analysis of this figure reveals the appearance of an anodic peak (I_{ap}^f) at ca. -190 mV vs. Ag/AgCl/KCl (sat.) at the Pt/GC electrode, during the forward scan, with a gradual decrease of the peak current, at potentials larger than ca. -190 mV . This decrease in the peak current may be attributed to the gradual formation of Pt oxide (see Fig. 43.2c) which is inactive towards methanol oxidation. Another anodic peak (I_{ap}^b) appears during the backward scan, which was assigned to the oxidation of methanol and/or methanol residues (e.g., CO) at the freshly reduced PtO surface [23, 24]. Interestingly, the modification of the Pt/GC electrode with NiOx has greatly enhanced its catalytic activity towards methanol oxidation (Fig. 43.4f). That is, the onset potential of methanol oxidation shifts by about ca. 100 mV to the negative direction of potential compared to that observed at the Pt/GC electrode concurrently with a significant increase in the peak current (I_p). The relative peak current density of $I_{\text{ap}}^f/I_{\text{ap}}^b$ can be used as an index to describe the tolerance of the electrode against the carbonaceous species poisoning [24]. A large ratio means a good tolerance of the anode against the poisoning species. This ratio increased from 4.875 at the Pt/GC electrode to 6.528 at the NiOx/Pt/GC electrode. This catalytic enhancement points to a crucial role of NiOx in the oxidation of methanol. The enhanced activity of NiOx/Pt/GC for MEO in alkaline media can be attributed to

the synergistic role of Pt and nickel oxides/hydroxides in the catalytic enhancement. The poisoned Pt nanoparticles surface with CO_{ad} can be regenerated via the reaction of surface CO with nickel oxides/hydroxides on the catalyst surface [25, 26].

43.4 Conclusion

Nickel oxide (NiOx)-modified GC and Pt/GC electrodes were prepared electrochemically and tested towards FA, Gl, and ME oxidation in 0.3 M NaOH solutions. The NiOx/GC electrode exhibited a catalytic activity towards glucose and methanol oxidation but did not show any activity towards FA oxidation. However, the NiOx/Pt/GC electrode showed a superb activity towards the oxidation of FA, Gl, and ME in comparison to Pt/GC electrode. Generally, the superb catalytic activity of NiOx/Pt/GC electrode is attributed to the role of NiOx, which could provide the necessary oxygen species to the catalyst surface to accelerate the oxidative removal of poisoning materials at lower potential.

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