



Electrochemical synthesis of nickel–iron layered double hydroxide: Application as a novel modified electrode in electrocatalytic reduction of metronidazole



Kamellia Nejati ^{a,*}, Karim Asadpour-Zeynali ^b

^a Chemistry Department, Payame Noor University, PO. Box 19395-3697 Tehran, I.R. of Iran

^b Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz 51666-16471, Iran

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ABSTRACT

A new and simple approach based on the electrochemical method was used for preparation of reproducible nanostructure thin film of Ni/Fe-layered double hydroxides (Ni/Fe-LDH) on the glassy carbon electrode (GCE). The electrochemical behavior of the Ni/Fe-LDH deposited on GCE electrode is studied. Study of the scanning electron microscopy shows the formation of a nanostructure thin film on the glassy carbon electrode. Electrochemical experiments show that Ni/Fe-LDH modified glassy carbon electrode exhibits excellent electrocatalytic reduction activity with Metronidazole. The method was successfully applied for the analysis of Metronidazole in tablets. The results were favorably compared to those obtained by the reported BP method.

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1. Introduction

Layered double hydroxides (LDHs), known as anionic clays, consist of positively charged brucite-like host layers and can be described by the general formula as $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^{n-}_{x/n} \cdot yH_2O]^{x-}$, where M^{II} and M^{III} represent divalent and trivalent metal ions, A^{n-} being an n -valent anion [1,2]. Net positive charge on the layers is due to partial substitution of divalent metal ions (M^{II}) by trivalent ones (M^{III}), neutralized by the inter-layers composed of anions and water molecules [3]. LDHs can be easily and inexpensively synthesized under the laboratory conditions, with controllable chemical composition of the layer and interlayer domains [4]. Due to large specific surface areas, low memory effect, good biocompatibility, high chemical stability, adsorption property and catalytic activity, LDHs should be potentially attractive materials in different fields such as catalysis [5,6], electrodes for alkaline secondary batteries [7], nanotechnology [8,9], anion exchangers [10–12], adsorbents [10,13], scavengers for acids [14], polymer additives [15], antacids in medicine [16], electrode surface modifications and sensors [1,2]. Among all the chemical sensors reported in the literature, electrochemical sensors are more interesting, due to their considerable sensitivity, experimental simplicity, and low cost. For analytical applications, inorganic materials, such as LDHs, have attracted the attention of electrochemists, because of their wide range of compositions, adsorption

behavior and electrocatalysis properties with respect to analytes [17–20].

Very recently Tonelli et al. [1] have reviewed different methods used for the preparation of LDH films on various substrates, conductive properties of LDHs, applications in potentiometric anion analysis, early analytical applications of chemically modified electrodes (CMEs) based on the ability of LDHs to preconcentrate redox-active anions and the most recent applications of electrocatalytic properties of LFD-modified electrodes. In another recent report, Mousty and Prevot [2] have also reviewed the LDHs as electrode materials for electrochemical detection, and energy storage, specifically focusing on their application as a supercapacitor, an alkaline or lithium battery, and (bio-) sensor. The paper focuses particularly on the use of hybrid and biohybrid LDH materials in amperometric sensors and biosensors.

Heterocyclic nitro-compounds such as metronidazole are widely used as antibacterial and anticancer agents. Therefore, the development of methods that permit rapid and accurate determination of these components in drug formulations and biological samples is important. There are several analytical methods for the determination of MTZ such as spectrophotometry [21], high performance liquid chromatography [22], electrophoresis [23], and voltammetry [24–26].

To the best of our knowledge, there is not any report on application of Ni/Fe-LDH modified electrode for electrocatalytic reduction of components. In the present work, Ni/Fe-LDH was synthesized simply via electrodeposition method on glassy carbon electrode and its voltammetric behavior is investigated. Then, the LDH modified electrode was used for the electrocatalytic reduction and determination of metronidazole (MTZ).

* Corresponding author. Tel.: +98 411 5412118; fax: +98 411 5412108.

E-mail addresses: k_nejati@pnu.ac.ir, nejati_k@yahoo.com (K. Nejati).

2. Experimental

2.1. Apparatus and software

All electrochemical experiments were performed with BHP2063 + Electrochemical Analysis System (Behpajoo, Iran) interfaced with a personal computer. A three-electrode cell, containing a modified glassy carbon electrode (2 mm in diameter) with Ni/Fe-LDH, a Saturated Calomel Electrode (SCE) as reference electrode and a platinum wire auxiliary electrode were used. All potentials in the text refer to SCE (counter and reference electrodes obtained from Azar Electrode Co., Urmia, Iran). The pH measurements were carried out by means of Metrohm pH-Meter 691. The X-ray diffraction (XRD) patterns were recorded with a Bruker AXS model D8 Advance diffractometer using Cu- $K\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$), with the Bragg angle of $6\text{--}70^\circ$ and performing steps of 0.04° (2θ) and counting 4 s/step. The Field Emission Scanning Electron Microscopy (FESEM)/Energy Dispersive X-ray Analysis (EDAX) was performed using a Hitachi S4160 Field Emission Scanning Electron Microscope equipped with an EDAX system. The accelerating voltage was 10 kV with the beam current of 1 nA and the spectra collection time of 100 s.

2.2. Reagents and standard solutions

All reagents were of analytical grade. The water utilized in all studies was double distilled and deionized. Tablets of metronidazole were taken from an Iranian pharmaceutical company (Tehran Pars Company). The amount of 10^{-3} M solution of metronidazole was freshly prepared and used as the stock solution by dissolving it in water by ultrasonic waves. These solutions were diluted up to the required concentrations with the same solvent. Britton–Robinson (B–R) buffer (0.1 M) was prepared by dissolving appropriate amounts of boric acid, orthophosphoric acid and glacial acetic acid in water and adjusting to the desired pH value with sodium hydroxide.

2.3. Preparation of real samples

Contents of ten MTZ tablets, labeled with amount of 250 mg per tablet, were completely powdered and amount of average weight of one tablet was weighted. For preparation of spiked samples, 250.0 mg of powders and 250.0 mg of standard sample were accurately weighted and dissolved with ultrasonication in 50 ml of water solution. 500 μl of the resultant solution was diluted in 10 ml buffer and it was used for electrochemical determinations. The standard addition method was used for the determination of MTZ in real samples.

2.4. Preparation of the modified electrode

Prior to modification, the bare glassy carbon electrode was polished with alumina powder of $0.05 \mu\text{m}$ diameter on a wet polishing cloth. After each polishing, the electrode was sonicated in doubly distilled water for 10 min in order to remove any adsorbed substances. Finally, it was dried with acetone. A Ni/Fe-LDH film was electrochemically generated on the cleaned GC electrode at a optimum constant potential of -0.9 V for 90 s in an aqueous solution containing $\text{Ni}(\text{NO}_3)_2$ 0.12 M, $\text{Fe}(\text{NO}_3)_3$ 0.04 M and KNO_3 0.15 M. The pH of this solution was 3. After modification, the electrode was thoroughly rinsed with water and kept at room temperature for further use.

3. Results and discussion

3.1. Characterization of the modified Ni–Fe-LDH

The preparation of the Ni/Fe-LDH modified glassy carbon electrode was carried out in a single step involving the electrochemical deposition of Ni/Fe-LDH on the GCE surface. This procedure may have been done by

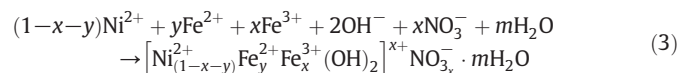
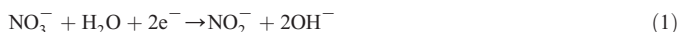
amperometry or cyclic voltammetry technique using optimized conditions such as $\text{Ni}^{2+}:\text{Fe}^{3+}$ ratio, concentrations, applied potential and electro-plating time. Preliminary experiments showed that the modified electrodes with amperometry technique have better electrocatalytic ability, higher stability and reproducibility. Also, after preparation of the modified electrode the obtained cyclic voltammograms in buffer solution were found to be sharper. Therefore, amperometry technique was used for the preparation of modified electrode and the effective parameters were optimized.

The measured XRD pattern of the film, for a deposition time of 200 s, is shown in Fig. 1. It is characterized by a low signal to noise ratio, due to the low amount of the LDH material on the electrode surface. As shown in Fig. 1, LDH displays the characteristic (003), (006), (012) and (110) reflections corresponding to hydrotalcite-like materials which also establishes the purity of the Ni/Fe-LDH obtained from the electrodeposition. The basal spacing value (d_{003}) of LDH phase is approximately 0.86 nm, consistent with that of nitrate intercalated LDH materials [27,28]. The XRD pattern is related to a poor crystalline phase, probably due to the fast kinetics of the LDH precipitation which hinders an ordered stacking of the brucite layers.

The FESEM was employed to explore the morphology of the modified electrode. Fig. 2a shows the typical FESEM image of the Ni/Fe-LDHs film on glassy carbon electrode. The FESEM photograph of film obtained on the glassy carbon electrode is uniform, homogeneous and completely covering the electrode surface and also the LDH particles with size below 100 nm are shown in Fig. 2a.

The EDAX experiment was further performed to confirm the existence of the Ni/Fe-LDH on the electrode surface. From Fig. 2b it can be seen that Ni and Fe elements composed of Ni/Fe-LDH were present on the electrode surface.

The following reactions on the electrode surface may be performed in the preparation of modified electrode:



assuming that the formula of the Ni/Fe-LDH is expressed as $[\text{Ni}_{(1-x-y)}^{2+}\text{Fe}_y^{2+}\text{Fe}_x^{3+}(\text{OH})_2]^{x+} \text{NO}_3^- \cdot m\text{H}_2\text{O}$ [29].

Fig. 3 shows the typical cyclic voltammogram of Ni/Fe-LDH electrode in solution pH of 11.5 with scan rate of 50 mV s^{-1} . A pair of well-

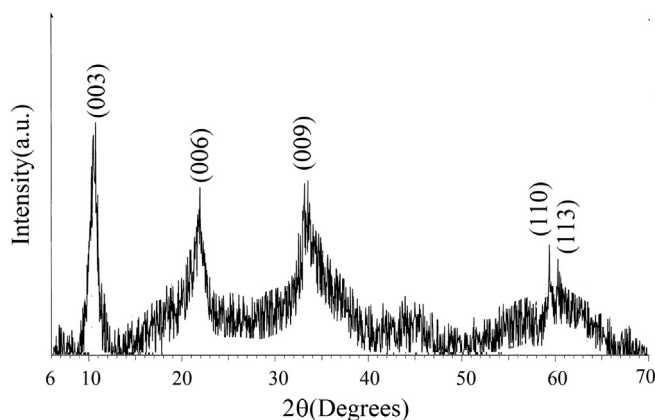


Fig. 1. The XRD patterns for Ni/Fe-LDH.

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