Electrochemical determination of rutin by using NiFe₂O₄ nanoparticles-loaded reduced graphene oxide

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ABSTRACT

A binary transition metal oxide containing nickel and iron (NiFe₂O₄) and hybridization of this nanomaterial with reduced graphene oxide (rGO) are synthesized by the hydrothermal method. X-ray diffraction (XRD) and Raman spectroscopy confirm the successful synthesis of these materials. Also, scanning electron microscope (SEM) and transmission electron microscope (TEM) images illustrated the particle morphology with the particle size of 20 nm. The synthesized material is then examined as a sensor on the surface of the glassy carbon electrode to detect a very small amount of rutin. Some electrochemical tests such as cyclic voltammetry, differential pulse voltammetry (DPV), and impedance spectroscopy indicate the remarkable accuracy of this sensor and its operation in a relatively wide range of concentrations of rutin (100 nM–100 μM). The accuracy of the proposed electrochemical sensors is approximately 100 nM in 0.1 M PBS, (pH = 3) which is relatively impressive and can be reported. Also, the stability rate after 100 DPV was about 95 %, which is a considerable and relatively excellent value. Considering the very good results, it seems that the NiFe₂O₄-rGO can be considered as a new proposal in the development of accurate and inexpensive electrochemical sensors.

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1 Introduction

The extensive use of rutin in clinical treatments has received much attention [1, 2]. Rutin has antibacterial [3], antiviral [4], anti-tumor [5], and anti-inflammatory [6] properties. Furthermore, it has effective physiological functions and has an effective role in diluting the blood [7] and lowering blood pressure [8]. Recently, in some countries, this drug has been included in the coronavirus treatment protocol in the current pandemic [9]. Therefore, the detection of rutin with a simple, rapid, and low-cost sensing method seems necessary.

So far, various methods such as capillary electrophoresis [10], chemiluminescence [11], sequential injection analysis [12], and electrochemical techniques have been used to determine the exact amount of rutin. But among them, the use of electrochemical techniques and the design of a sensor with an electrochemical approach is recommended due to its speed, accuracy, and very low cost [13, 14]. A review of scientific reports indicates different electrochemical sensors with accuracy that have been considered by the detection of rutin. In the structure of these sensors, precious and rare metals such as platinum, palladium, etc. have been used. Their disadvantage, in addition to the high cost, is the complex electrochemical mechanisms in the detection of rutin. Other problems are the very rapid oxidation of these materials and their failure and saturation after several times of detection [15–17].

The design and manufacture of sensors with low cost, high stability, and good anti-interference capability for rutin detection are very significant today. Binary transition metal oxides (BTMO) such as NiCo_2O_4 [13], CoFe_2O_4 [7], ZnFe_2O_4 [18], etc. in the form of AB_2O_4 are very popular in electrochemistry. For example, there are many reports on applications in supercapacitor electrodes, hydrogen evolution reaction [19], methanol oxidation [20], urea oxidation [21], supercapacitor [22], etc. In most of the mentioned applications, the good reason for the efficiency of these materials is the synergistic effect between two metal oxides. At the same time, these amazing materials have a very important problem, which is their very low electrical conductivity [23].

Nickel and iron have always been considered as two inexpensive and environmentally friendly elements in electrochemical applications [24–26]. It is clear that a suitable electrode for accurate detection of

various drugs, in addition to a high surface area, must also have a very good conductivity, but BTMOs do not have this advantage [27, 28]. Today, the use of carbonaceous materials such as reduced graphene oxides is very popular due to the high surface area and very good conductivity of these materials [29, 30].

One of the most important applications of graphene and its derivatives is the widespread use of this two-dimensional material in the field of energy. The unique properties of this material, including excellent conductivity and excellent mechanical and thermal properties, have made this material very important in the field of electrochemistry [31–34]. Metal oxides have also recently received much attention in the field of catalysis and electrochemistry. In many applications of metal oxides, due to the low electrical conductivity of these materials, a hybrid or composite of them is synthesized with rGO or conductive ionic liquids to solve the low conductivity of these materials [35–38].

In this research, a BTMO nanoparticle, NiFe_2O_4 , is synthesized, and to increase its specific surface area and conductivity, it is hybridized with reduced graphene oxide. The synergistic effect between the two metal oxides and rGO shows good in vitro results of the detection of rutin in the range of 0.01–00 μM by NiFe_2O_4 -rGO. The result confirms the widespread use of BTMOs hybridized with rGO as a biosensor in the field of bioelectrochemistry.

2 Experimental

2.1 Synthesis of NiFe_2O_4 and NiFe_2O_4 -rGO

After synthesizing graphene oxide by Hummers' method [39], NiFe_2O_4 and NiFe_2O_4 -rGO were synthesized by an easy hydrothermal method. The synthesis method is as follows: 2.5 mmol nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and 5 mmol iron (III) chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were dissolved in 50 ml deionized water and stirred for 10 minutes by sonicating, and then 20 mmol sodium acetate (CH_3COONa) was added in the above solution and stirred for 30 minutes. The solution was injected into the 100 ml stainless steel reactor, and the reaction was continued in the oven at 180°C for 24 hours. After that, the resulting material was washed with deionized water and ethanol

several times and calcinated at a temperature of 300°C for 2 hours. The resulting powder is NiFe_2O_4 .

The synthesis of the NiFe_2O_4 -rGO was performed with the same method, with the difference that at the first, a certain amount of GO was added to the mentioned nickel and iron sources. XRD and Raman spectroscopy analyses were performed to confirm the synthesis of NiFe_2O_4 and NiFe_2O_4 -rGO. Also, the morphology and the size of these materials were examined with scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2.2 Material characterization

The XRD analysis of rGO, NiFe_2O_4 , and NiFe_2O_4 -rGO was conducted BY XRD 3000 EQUINOX INEL with CuK α lamp to confirm the synthesis and study the crystal structure. As predicted, in Fig. 1, the presence of two relatively wide peaks at angles of about 25° and 43° confirms the successful synthesis of rGO. In the 2 θ of 18.4°, 30.3°, 35.7°, 43.2°, 53.8°, 57.4°, 63.2°, and 74.6°, there are characteristic peaks that belong to (111), (220), (311), (400), (422), (511), (440), and (533) planes, respectively, which confirm the successful synthesis of NiFe_2O_4 that is in full compliance with JCPDS (Card No. 10–0325) [40]. Using the Scherrer equation ($t = \frac{0.9\lambda}{\beta \cos \theta}$), the size of nanoparticles is estimated to be about 20 nm, which is also consistent with the TEM results. What is clear and seen in similar works is, in most cases with the combination of nanoparticles and graphene, the amount of crystallinity is reduced. Figure 1 shows that some NiFe_2O_4 peaks disappear when it

hybridized with rGO, and others peaks are slightly shifted by overlapping with rGO characteristic peaks [41].

One of the most important analyses that are always important for carbon composites is Raman spectroscopy. Raman spectra were collected with Thermo Nicolet Almega XR Raman. Figure 2 shows the Raman spectrum of rGO with two peaks at 1594 and 1354 cm^{-1} , known as the D-band and the G-band, respectively. The D and G bands belong to the defects and sp^3 carbon, respectively. In the NiFe_2O_4 -rGO spectrum (Fig. 2), two peaks are specified in the Eg vibration states at 336 and 666 cm^{-1} . Also, the T_{2g} vibration mode is specified at 497 cm^{-1} . In addition to the aforementioned peaks, the A1g vibration mode has also appeared at 574 and 706 cm^{-1} . The relative intensity ratio of (I_D/I_G) was 0.76 for rGO and it was increased to 0.83 for NiFe_2O_4 -rGO. The reason is that introduction of NiFe_2O_4 -rGO increased the intensity of local defects and disorders [42, 43]. The compatibility of the peaks shown in NiFe_2O_4 with other studies confirms its successful synthesis [40, 44].

SEM images related to rGO, NiFe_2O_4 , and NiFe_2O_4 -rGO are shown in Fig. 3a–c, respectively. These images were prepared to study the morphology and size of the synthesized nanomaterials. As can be seen in Fig. 3a, graphene nanosheets have a clear two-dimensional morphology. Figure 3b shows the spherical morphology of NiFe_2O_4 nanoparticles. In Fig. 3c, these nanoparticles are uniformly placed on the surface of rGO plates.

Fig. 1 The Raman spectra of rGO, NiFe_2O_4 , and NiFe_2O_4 -rGO

Fig. 2 The Raman spectra of rGO and NiFe_2O_4

◀ **Fig. 3** SEM micrographs of rGO (a), NiFe₂O₄ (b), and NiFe₂O₄-rGO (c), EDX mapping of NiFe₂O₄ (d), and BET of rGO, NiFe₂O₄, and NiFe₂O₄-rGO (e)

To prove this uniform dispersion, the Energy dispersive X-ray (EDX) mapping analysis was done and the results are shown in Fig. 3d. EDX mapping images confirm the uniform dispersion of NiFe₂O₄ nanoparticles on the surface of rGO and also approve the presence of nickel, iron, oxygen, and carbon in the structure of this nanohybrid.

The specific surface area and porosity are very important features of hybrid composites for biosensor applications. In this study, the surface of nanomaterials was calculated by the Brunauer-Emmett-Teller (BET) surface area analysis (Fig. 3e). Increasing the surface area increases the active sites in the nanomaterials and makes redox reactions easier. The addition of rGO to NiFe₂O₄ increases the surface area of NiFe₂O₄-rGO to 187.2 m² g⁻¹. Also, the specific surface area is 91 m² g⁻¹ for rGO and 111 m² g⁻¹ for NiFe₂O₄.

Figure 4a-c indicate the TEM images of rGO, NiFe₂O₄, and NiFe₂O₄-rGO, respectively. As can be seen in Fig. 4a, transparent graphene sheets are very thin and also indicate the few layers. Figure 4b shows the TEM image of NiFe₂O₄ nanoparticles. The particle size in this image is about 20 nm, which is compatible with the XRD results. Figure 4c also shows the uniform placement of the NiFe₂O₄ nanoparticles on the surface of transparent rGO plates. The incorporation of NiFe₂O₄ in rGO can provide active sites, increase

the dispersion of nanoparticles, and prevent agglomeration.

2.3 Electrochemical characterizations

0.01 g of each of NiFe₂O₄ and NiFe₂O₄-rGO was dissolved by sonication in a solution of Nafion and isopropyl alcohol/water (70:30) for 20 min. Then, 10 µL of the resulting slurry (equivalent to one drop) was placed on the surface of a glassy carbon electrode (GCE) and dried at room temperature. The GCE electrode modified by each of the NiFe₂O₄ and NiFe₂O₄-rGO nanomaterials will act as the working electrode. Ag/AgCl and platinum wire (0.5 mm diameter) were used as the reference and auxiliary electrodes, respectively. The modified electrode was dried for 1 hour at 40°C, and the sensitivity of the nanomaterials was examined for rutin detection.

As mentioned, one of the most important reasons for adding rGO to the NiFe₂O₄ structure was to increase the conductivity as well as the effective surface area. The increase in the active surface area, as shown in the BET, was achieved by adding rGO. Figure 5a shows cyclic voltammetry of NiFe₂O₄ and NiFe₂O₄-rGO in 0.1 M KOH solution at the potential range of 0 to 500 mV. A redox peak in both diagrams is indicated. Increasing the current density as well as decreasing the overpotential in the graphene-containing electrode confirms the increase in electrode conductivity by adding rGO to the structure of NiFe₂O₄.

Impedance analysis was also performed on the electrodes containing rGO and without it. In this analysis, the semicircle diameter indicates Rct, which

Fig. 4 The TEM images of rGO (a), NiFe₂O₄ (b), and NiFe₂O₄-rGO (c)

Fig. 5 CV curves (a) and EIS plots (b) of NiFe₂O₄ and NiFe₂O₄-rGO

represents the resistance to the charge transfer. As shown in Fig. 5b, the R_{ct} in NiFe₂O₄-rGO is 65 Ω and in NiFe₂O₄ is 116 Ω , showing increasing of conductivity by adding rGO to the NiFe₂O₄. Thus, NiFe₂O₄-rGO/GCE electrode was selected as the working electrode and other rutin detection tests were performed with this electrode.

3 Effect of pH in rutin detection

To investigate the mechanism of rutin electro-oxidation, CV analysis in different pHs was performed at PBS 0.1 M at a scan rate of 20 mV/s. As shown in Fig. 6a, the anodic peak current of rutin oxidation (I_{pa}) has increased when pH changed from 1 to 2, and the increase in I_{pa} from pH 2 to 3 is relatively highly significant. The current density at pH 3 reaches the maximum value, then the current density gradually decreases with increasing pH value from 3 to 6. Then, by selecting pH 3, as the most suitable pH, the sensitivity of the proposed sensor for very low concentrations and also the effect of scan rate on the rutin electro-oxidation process will be investigated. At low pHs, the peak current increases due to the electrostatic interactions between the negative charge of the NiFe₂O₄/rGO and the positive charge of rutin. At high pHs, the degree of protonation of rutin reduces resulting in less interaction between electrode and electrolyte.

4 Effect of scan rate on rutin detection

To investigate the effect of the scan rate on the rutin oxidation process, the CV test of NiFe₂O₄-rGO/GCE electrode was performed at different scan rates (20 to 200 mV/s) in 0.1 M PBS (pH 3) and 1 μ M rutin. As shown in Fig. 6a, redox peaks become sharper as the scan rate increases. With increasing scan rate, the peak potential tends to positive values, indicating that the reaction is quasi-reversible. As we know, I_{pa} and I_{pc} are the maximum current density at the forward and backward scan, respectively. Figure 6b shows that I_{pa} and I_{pc} are simultaneously increasing with the increase in the scan rate. By drawing the log I_{pa} during oxidation as well as the log I_{pc} during a reduction according to log v , two equations are obtained from the following equations:

$$\log I_{pa} = -0.34 + 0.84 \log v \quad (1)$$

$$\log I_{pc} = 0.44 - 0.84 \log v \quad (2)$$

The logarithmic diagram of I_{pa} and I_{pc} according to the logarithm v shown in Fig. 6c. This diagram shows the linear relationship between log I_{pa} and log v with $R^2 = 0.982$ and log I_{pc} with log v with $R^2 = 0.981$. As is clear, the slope is between 0.5 and 1, representing that both diffusion and adsorption processes simultaneously control the electrochemical reactions. In Fig. 6d, the I_{pa} and I_{pc} diagrams are plotted in terms of a square root of the scan rate ($v^{1/2}$). The calculation of the regression line for I_{pa} and I_{pc} shows $R^2 = 0.917$, indicating that the diffusion-controlled process is dominant in the rutin detection.

Fig. 6 The CV curves of NiFe₂O₄-rGO at different pHs (a) and various scan rates (b) and log I_{pa} and I_{pc} versus log scan rate (c) and the square root of scan rate (d)

4.1 Quantitative analysis of rutin by DPV

To evaluate the sensitivity of NiFe₂O₄-rGO electrode for measuring very small amounts of rutin, differential pulse voltammetry (DPV) analysis was performed in 0.1 M PBS, (pH 3) and the concentration range of 100 μM to 100 nM rutin (Fig. 7a). As it is clear, I_{pa} decreases with decreasing rutin concentration, and finally reaches a minimum at a concentration of 100 nM, and there is almost no current at concentrations below 100 nM. In general, it can be said that the detection limit of the proposed sensor is 100 nM rutin, which is almost a competitive and appropriate value compared to previous works [13, 45–49]. The good sensitivity results can be related to the synergistic effect between rGO and NiFe₂O₄

nanoparticles. Drawing I_{pa} graph according to rutin concentration and obtaining the equation with regression $R^2 = 0.99$ indicates the linearity of the relationship and the satisfactory results (Fig. 7b). Also, to evaluate the stability of this proposed electrochemical sensor, DPV analysis was performed 100 times at a rutin concentration of 100 nM in 0.1 M PBS, (pH 3). The results show that I_{pa} decreases less than 5 % after 100th (Fig. 7c), which confirms the relatively good stability of the proposed sensor. The comparison of the analytical performance of NiFe₂O₄-rGO with other electrochemical methods for rutin determination was listed in Table 1.

Fig. 7 DPV curves of NiFe₂O₄-rGO at different concentrations of rutin (a) the plot of current density versus rutin concentration (b) and DPV curves at first and 30th cycle (c)

Table 1 The comparison of the analytical performance of NiFe₂O₄-rGO with other electrochemical methods for rutin determination

Electrode	Method	Linear range	Reference
NiCo ₂ O ₄ /rGO	DPV	0.1–8 and 8–150 μM	[13]
MB@ZIF-8/RGO/GCE	DPV	0.1–100 μM	[50]
Mg-Al-Si@PC/GCE	DPV	1–10 μM	[51]
CeO ₂ /GCE	DPV	0.5–500.0 μM	[52]
GR-MnO ₂ /CILE	DPV	0.01–500.0 μM	[53]
NiFe ₂ O ₄ -rGO	DPV	100 nM–100 μM	This work

According to previous researches, the mechanism of rutin oxidation is containing a two-electron/two-proton oxidation process, which takes place in several stages [46]. The mechanism is shown in Fig. 8. At the first, a phenoxy radical (the most stable form is shown in Fig. 8) is created by electron transfer, and then a carbocation is created during a second electron transfer. After that, 3',4'-diquinone is obtained by

dehydration of the carbocation, and then it is reduced to rutin during the reverse reaction.

5 Conclusions

BTMOs are very popular in electrochemical applications. In summary, in this study, NiFe₂O₄ and NiFe₂O₄-rGO nanocomposites were synthesized, and

Fig. 8 Schematic of rutin oxidation

the application of this nanostructure in rutin detection was investigated. The excellent accuracy of this electrochemical sensor in rutin detection, as well as its low cost and very simple and accurate operation, has made it a tempting option for detecting very small amounts of rutin. NiFe₂O₄-rGO can be detected for low concentrations of rutin (100 nM) and also the stability rate after 100 differential pulse voltammetry (DPV) was about 95 %, which is an excellent value.

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