

NiO/CNTs Nanocomposite Modified Ionic Liquid Carbon Paste Electrode as a Voltammetric Sensor for Determination of Quercetin

Vinod Kumar Gupta^{1,2,*}, Fereshteh Golestani,³ Saeid Ahmadzadeh⁴, Hassan Karimi-Maleh^{3,5,*}, Gozal Fazli⁶, Sahebe Khosravi⁷

¹ Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India

² Center for Environment and Water, The research Institute, King Fahd University of Petroleum and Minerals Dhahran, Saudi Arabia

³ Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran

⁴ Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran

⁵ Department of Chemistry, Mazandaran Science and Research Branch, Islamic Azad University, Mazandaran, Iran

⁶ Department of Biology, Faculty of Science, Gonbad Kavous University, Gonbad Kavous, I. R. Iran.

⁷ Department of nanophysics, Institute of Science and High Technology and Environmental Sciences, Graduate University of Advanced Technology

*E-mail: vinodfcy@gmail.com (V.K. Gupta); h.karimi.maleh@gmail.com (H. Karimi-Maleh)

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A high sensitive carbon paste electrode modified with NiO/CNTs and ionic liquid (ILs/NiO/CNT/CPE) was describe for voltammetric determination of quercetin. Compared to unmodified carbon paste electrode, the electrochemical response was greatly improved for quercetin electrooxidation. Result shows, the oxidation peak current was increased to about 6.5 times at the surface of ILs/NiO/CNT/CPE compared to CPE. The linear response range and detection limit were found to be 0.08–400 μM and 0.03 μM , respectively. ILs/NiO/CNT/CPE was successfully applied for the determination of quercetin in real samples such as onions, apple and capsule. The results showed that the proposed method is highly selective, sensitive with a fast response for quercetin analysis.

Keywords: Quercetin; NiO/CNTs nanocomposite; Ionic liquids; Modified electrode

1. INTRODUCTION

Quercetin is a flavonoid widely distributed in nature. It is a naturally occurring polar auxin transport inhibitor [1]. Quercetin is an effective bronchodilator and helps reduce the release of

histamine and other allergic or inflammatory chemicals in the body [2]. Also, laboratory studies have investigated quercetin's potential for use in anti-cancer applications [3]. Several methods have been proposed for the determination of AA such as spectrophotometry [4], high performance liquid chromatography [5, 6], chemiluminescence [7], capillary electrophoresis [8] and electrochemical methods [9, 10].

Room temperature ionic liquid modified electrode has been widely used in the electroactive compounds analysis owing to its unique electrochemical properties, including higher ionic conductivity, wider electrochemical windows and low cost [11-16]. This kind of modified electrode has gained increasing attention recently due to their potential applications to develop high performance electrochemical sensors [16-25]. On the other hand, coupling of room temperature ionic liquid and nanomaterials for modification of electrodes have several advantages over traditional room temperature ionic liquid modified electrodes, including improved sensitivity, compatibility and stability [26-31].

Nanoscale based materials such as carbon nanotubes, graphene, nanoparticles, nanocomposite are being used for several electroanalytical applications [32-37]. Electrochemical analysis using modified electrode is taking advantages from all the possibilities offered by nanocompounds easy to be detected by conventional electrochemical methods [38-42].

According to the above points, it is very important to create suitable conditions for the quercetin analysis of in food and pharmaceutical samples. Therefore, in continuation of our studies on the preparation of chemically modified electrodes [43-46], a novel ILs/NiO/CNT/CPE for the voltammetric determination of quercetin was investigated using square wave voltammetry.

2. MATERIAL AND METHODS

2.1. Chemicals and Apparatus

All chemicals were of analytical grade and were used as received without any further purification. Quercetin was procured from Sigma-Aldrich. All voltammetry and chronoamperometry measurements have been performed on μ -Autolab with PGSTAT (Eco Chemie, the Netherlands). A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl/KCl_{sat} electrode as a reference electrode was used. The working electrode was a CPE, ILs/NiO/CNT/CPE, ILs/CPE or a NiO/CNT/CPE. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-K α radiation ($k = 1.54 \text{ \AA}$).

2.2. Synthesis of NiO/CNTs nanocomposite

The preparation of NiO/CNTs catalysts includes three steps. First, the chemical pretreatment of carbon nanotubes is required. A definite amount of carbon nanotubes was introduced into 80 mL of nitric acid and sulfuric acid (3 : 1 in volume) solution, then 10 mL of ethanol were dropped into the solution slowly, and the solution was agitated in a shaker at 70 °C and 200 rpm for 24 h. In the second

step, certain amounts of purified CNTs (6 g) were dispersed into distilled water solution of NaOH (0.5 M, 100 mL) by ultrasonication for 20 min. The third step is the supporting of nickel oxide on the carbon nanotubes by a direct deposition process. 6.0 g $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 100 mL of distilled water. In the constant magnetic stirring, the solution of $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was added drop wise to the solution of CNTs at 50°C through a dropping funnel. The rate of addition of the salt solution was kept approximately at 20 mL/h. After completion of the precipitation procedure, the mixture was stirred at room temperature for 12 h, washed and filtered continually in distilled water (pH 8.0), and then dried at 120°C . Finally, the solid samples were calcined at 350°C for 2 h.

2.3. Preparation of the modified electrode

ILs/NiO/CNT/CPE was prepared by mixing 0.2 g of 1-methyl-3-butylimidazolium bromide, 0.6 g of liquid paraffin, 0.3 g of NiO/CNTs and 0.9 g of graphite powder. Then the mixture was mixed well for 45 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into a glass tube as described above to prepare ILs/NiO/CNT/CPE. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper.

3. RESULTS AND DISCUSSION

3.1. Characterization of nanocomposite

NiO/CNT nanopowders were analyzed by XRD analyses (Fig. 1). The XRD pattern of NiO/CNT nanopowders, in the 2θ range of $10\text{--}80^\circ$, is shown in Fig. 1. It clearly proves the presence of NiO nanoparticle, with a diffraction peak at about 26° from CNTs. An average diameter of as-synthesized NiO nanoparticle was calculated from the broadness peak of $2\theta=35.6$ by using Scherrer equation ($D = K\lambda/\beta \cos\theta$), and it is about 22.0 nm. The morphology of the as-grown nanostructures was characterized by SEM. Typical SEM micrograph of the NiO/CNTs is shown in Fig. 2. The results show the presence of NiO nanostructure grown on carbon nanotubes.

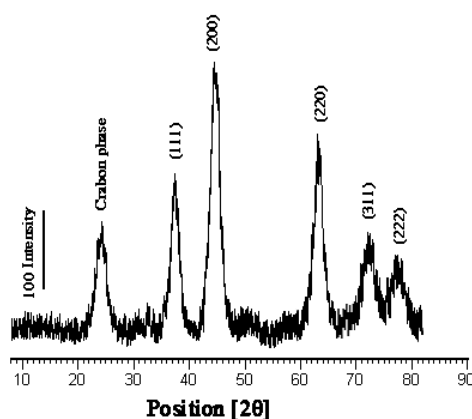


Figure 1. XRD patterns of as-synthesized NiO/CNT nanocomposite

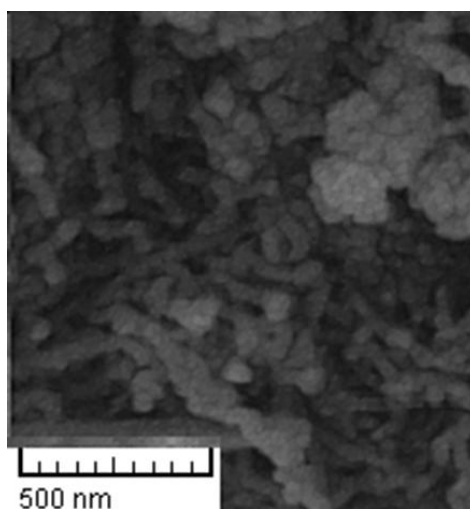


Figure 2. SEM image of NiO/CNTs synthesis in this work.

3.2. Modification electrode effect on electrochemical response

The active surface area of the modified electrode was estimated according to the slope of the I_p versus $v^{1/2}$ plot for a known concentration of $K_4Fe(CN)_6$, based on the Randles–Sevcik equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C_0 \quad (1)$$

where I_p refers to the anodic peak current, n the electron transfer number, A the surface area of the electrode, D_R the diffusion coefficient, C_0 the concentration of $K_4Fe(CN)_6$ and v is the scan rate. The microscopic areas were calculated from the slope of the $I_p-v^{1/2}$ relation (taking concentration of $K_4Fe(CN)_6$ as 1.0 mmol L^{-1} , concentration of KCl electrolyte as 0.10 mol L^{-1} , $n = 1$, $D_R = 7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The results obtained were 0.25 and 0.09 cm^2 for ILs/NiO/CNT/CPE and CPE, respectively. The results further show that the presence of NiO/CNTs and ILs together contributed to an increase in the active surface area of the electrode.

The oxidation peak current of quercetin is closely related to the pH value of electrolyte solution. Therefore, the effect of pH was investigated using cyclic voltammetry technique. In order to ascertain this, the voltammetric response of quercetin at a surface of ILs/NiO/CNT/CPE was obtained in solutions with varying pH. It was found that the oxidation peak current increased gradually from pH 5.0 to 7.0, and then the current conversely decreased when the pH value increased from 7.0 to 8.0 (Fig. 3). So pH 7.0 was chosen as the optimal experimental condition.

The direct electrochemistry of quercetin on the modified electrode was investigated by square wave voltammetry. ILs/NiO/CNT/CPE exhibited significant oxidation peak current of $7.5 \mu\text{A}$ (Fig. 4, curve a). In contrast, low redox activity peak was observed at NiO/CNT/CPE (Fig. 4, curve c) and at unmodified CPE (Fig. 4, curve d) over the same potential range. The quercetin oxidation peak current at NiO/CNT/CPE and at CPE observed was around 2.5 and $1.15 \mu\text{A}$, respectively. In addition, at the surface of ILs/CPE, the oxidation current was about $5.0 \mu\text{A}$.

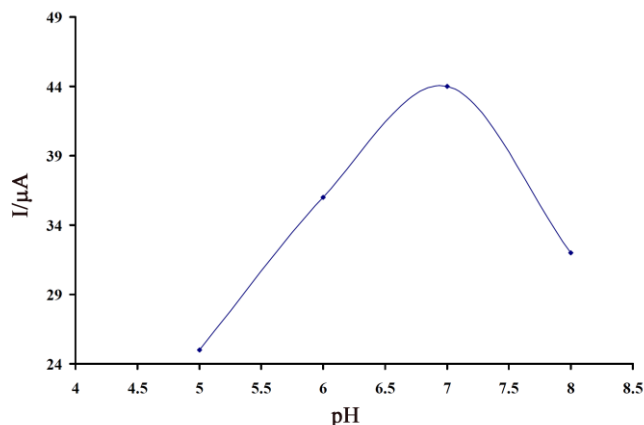


Figure 3. Current–pH curve for electrooxidation of 300 μM quercetin at ILs/NiO/CNT/CPE with a scan rate of 100 mV s^{-1} in cyclic voltammetry.

This indicated that the presence of ILs in CPE could enhance the peak currents. A substantial negative shift of the current starting from the oxidation potential for quercetin and dramatic increase of current of quercetin indicated the catalytic ability of ILs/NiO/CNT/CPE to quercetin oxidation. The results indicated that the presence of NiO/CNTs on ILs/NiO/CNT/CPE surface had great improvement on the electrochemical response, which was partly due to the excellent characteristics of NiO/CNTs such as good electrical conductivity, high chemical stability and high surface area. The suitable electronic properties of NiO/CNTs together with the ionic liquid gave the ability to promote charge transfer reactions, good anti-fouling properties, especially when mixed with a higher conductive compound such as ILs when used as an electrode.

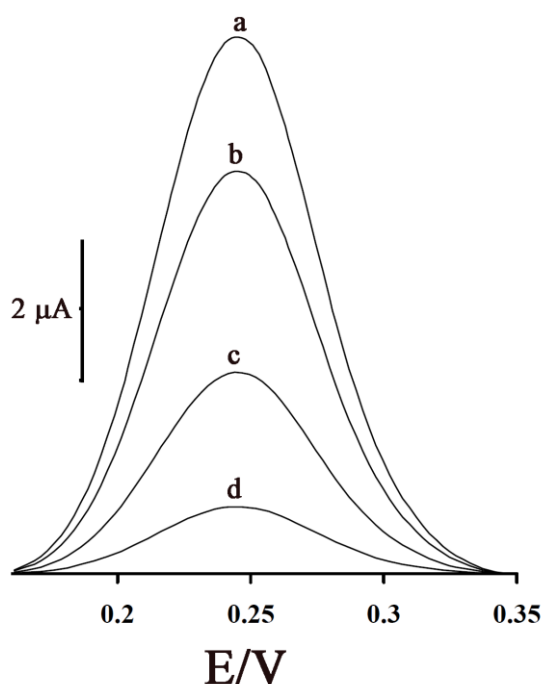


Figure 4. Square wave voltammograms of (a) ILs/NiO/CNT/CPE, (b) ILs/CPE, (c) NiO/CNT/CPE and (d) CPE in the presence of 300 μM quercetin at pH 7.0, respectively.

The effect of sweep rate (v) on peak potential (E_p) and peak current (i_p) of 400.0 μM quercetin in pH = 7.0 phosphate buffer solution was studied in the range of 25–200 mV s^{-1} at ILs/NiO/CNT/CPE. As can be seen in Fig. 5 inset, the recorded CVs showed a positive shift in E_p , which confirms the irreversibility of the electro-oxidation process. On the other hand, presence of a linear relationship between the peak current (i_p) and $v^{1/2}$ regarding following equation confirms the diffusion-controlled process for the electro-oxidation of quercetin on the surface of ILs/NiO/CNT/CPE in the studied range of potential sweep rates (Fig. 5) [53-56].

$$I_p = 9.4748 v^{1/2} - 39.880 \quad (r^2 = 0.9938, I \text{ in } \mu\text{A}, v \text{ in } \text{mV s}^{-1}) \quad (2)$$

In addition, the values of αn_α (n_α is the number of electrons involved in the rate determining step) was calculated for the oxidation of quercetin at pH 7.0 with ILs/NiO/CNT/CPE according to the following equation

$$\alpha n_\alpha = 0.048 / (E_p - E_{p/2}) \quad (3)$$

where $E_{p/2}$ is the potential corresponding to $I_{p/2}$. The value for αn_α was found to be 0.68 at the surface of ILs/NiO/CNT/CPE.

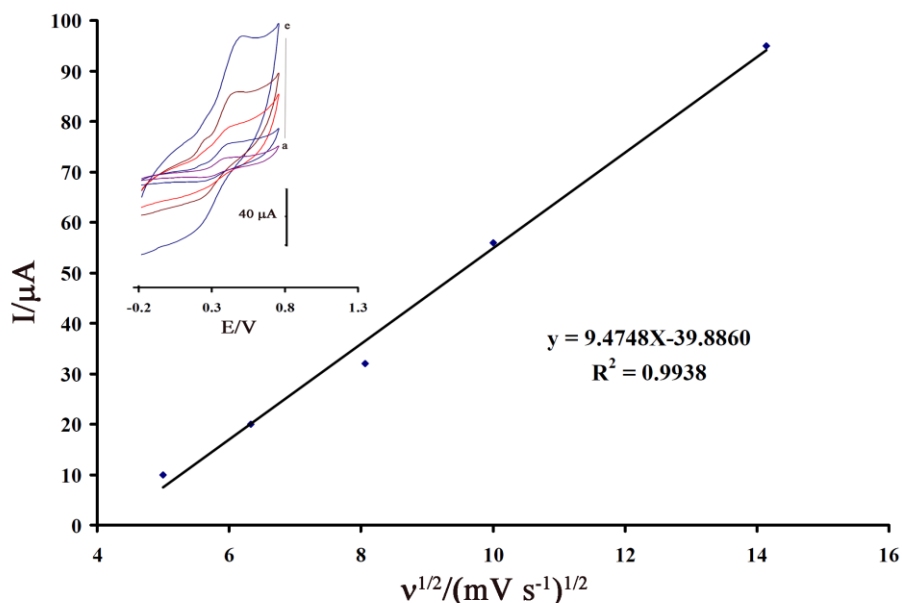


Figure 5. Plot of I_{pa} versus $v^{1/2}$ for the oxidation of quercetin at ILs/NiO/CNT/CPE. Inset shows cyclic voltammograms of quercetin at ILs/NiO/CNT/CPE at different scan rates of a) 25, b) 40, c) 65, d) 100 and e) 200 mV s^{-1} in 0.1 M phosphate buffer, pH 7.0.

The obtained value shows that the overpotential of quercetin oxidation is reduced at the surface of ILs/NiO/CNT/CPE, and also the rate of electron transfer process is greatly enhanced. This phenomenon is thus confirmed by the larger I_{pa} values recorded during cyclic voltammetry at ILs/NiO/CNT/CPE [57-62].

The chronoamperometry as well as the other electrochemical methods was employed for the investigation of electro-oxidation of quercetin at ILs/NiO/CNT/CPE. Chronoamperometric measurements of quercetin at ILs/NiO/CNT/CPE were done (Fig. 6) for various concentrations of

quercetin. For an electroactive material (quercetin in this case) with a diffusion coefficient of D , the current for the electrochemical reaction (at a mass transport limited rate) is described by the Cottrell equation:

$$I = nFAD^{1/2} C_b \pi^{-1/2} t^{-1/2} \quad (4)$$

Under diffusion control, a plot of I versus $t^{-1/2}$ will be linear, and from the slope the value of D can be obtained. The mean value of the D was found to be $3.0 \times 10^{-5} \text{ cm}^2/\text{s}$.

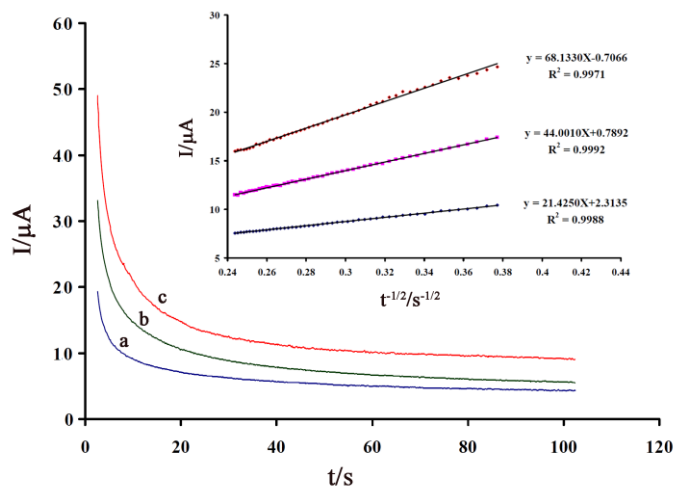


Figure 6. Chronoamperograms obtained at the ILs/NiO/CNT/CPE in the presence of a) 300; b) 400 and c) 500 μM quercetin in the buffer solution (pH 7.0). Inset) Cottrell's plot for the data from the chronoamperograms.

3.3. Analytical features

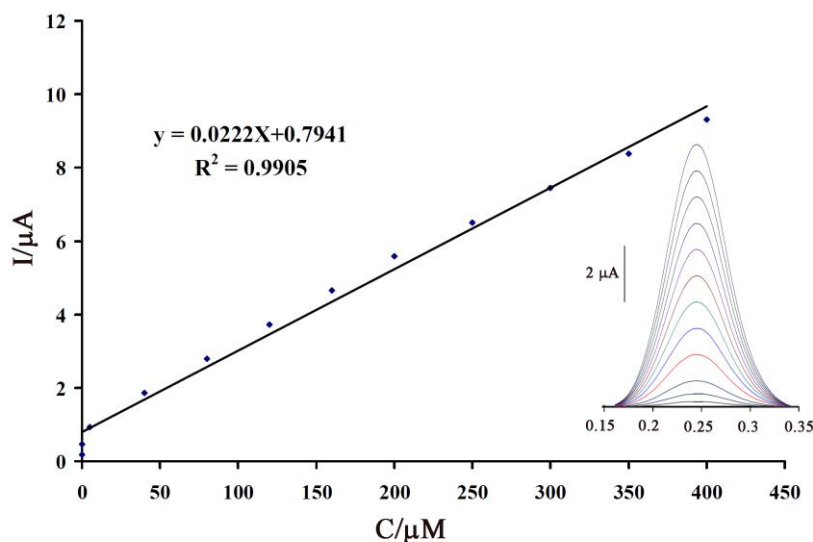


Figure 7. Plots of electrocatalytic peak current as a function of quercetin concentration in the range of b 0.08–400.0 μM . Inset) Square wave voltammograms of quercetin at a various concentrations.

Square wave voltammetry (SWV) was used to determine quercetin concentrations (Fig. 7 inset). The SW voltammograms clearly show that the plot of peak current versus quercetin concentration is linear for 0.08–400 μM of quercetin (Fig. 7). The detection limit was determined at 0.03 μM quercetin according to the definition of $Y_{LOD} = Y_B + 3\sigma$.

3.4. Stability and reproducibility of the sensor

Long-term stability is one of the most important properties for sensor application. The stability of ILs/NiO/CNT/CPE was investigated by SWV. The response currents can retain almost constant upon continuous 20 cyclic sweeps over the applied potential ranging from +0.15 to +0.35 V. After stored in refrigerator at 4°C for 45 days, the potentials of oxidation peak in SWVs remained at the same positions and the peak currents decreased by only about 3.3% of its initial current response. Furthermore, the reproducibility of the determination was performed with nine successive scans in the solution containing 20.0 μM . The RSD values were found to be 2.1% for the analyte, indicating good reproducibility of the modified electrode.

3.5. Interference studies

In order to evaluate the selectivity of the proposed sensor in the determination of quercetin, the influence of various foreign species on the determination of 10.0 μM quercetin was investigated. Tolerance limit was taken as the maximum concentration of foreign substances that caused an approximate relative error of $\pm 3\%$. The results are shown in Table 1. These results demonstrate that the propose sensor has a good selectivity for quercetin analysis in real samples.

Table 1. Interference study for the determination of 10.0 μM quercetin under the optimized conditions.

Species	Tolerante limits($W_{\text{Substance}}/W_{\text{quercetin}}$)
Glucose , Fructose, Lactose , Sucrose	1000
K^+ , ClO_4^- , Na^+ , Cl^- , CO_3^{2-} , Ca^{2+} , Mg^{2+} , SO_4^{2-}	700
Alanine, Serine, Aspartic acid, Threonine, Glycine, Valine, Methionine, Lucine, Alanine , Glycine, Phenylalanine	800
Starch	Saturation

3.6. Real Sample Analysis

In order to evaluate the analytical applicability of the proposed sensor, it was also applied to the determination of quercetin in food and pharmaceutical samples. Standard addition method was used for measuring quercetin concentration in the samples. The results given in Table 2 confirm that the modified electrode retained its efficiency for the determination of quercetin in real samples.

Table 2. Determination of quercetin in real samples.

Sample	Added (μM)	Expected (μM)	Founded (μM)	Recovery%
Apple	—	—	5.50 \pm 0.32	---
	4.50	10.0	9.63 \pm 0.44	96.3
Onions	—	—	20.22 \pm 0.38	—
	4.78	25.0	25.55 \pm 0.78	—
Capsule	—	5.0	4.85 \pm 0.44	97.0
	10.0	15.0	15.63 \pm 0.75	104.2

^a \pm Shows the standard deviation (n=5)

4. CONCLUSION

The ILs/NiO/CNT/CPE was developed for the rapid determination of quercetin. The ILs/NiO/CNT/CPE showed great improvement to the electrode process of quercetin compare to the traditional carbon paste electrode. Compared to traditional CPE, a decrease of overpotential of oxidation of quercetin with 6.5-fold increment in the oxidation peak current observed when using ILs/NiO/CNT/CPE as a new sensor. Under the optimum conditions in voltammetris determination, the oxidation peak current was proportional to the quercetin concentration in the range of 0.08–400 μM with the detection limit of 0.03 μM . Finally, the propose sensor was successfully used for the determination of quercetin in real samples.

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