Anal. Bioanal. Electrochem., Vol. 9, No. 6, 2017, 784-792

Analytical & Bioanalytical Electrochemistry

Full Paper

Kojic Acid Analysis in Foodstuff using a Reduced Graphene Oxide/NiO Nanocomposite Modified Electrode

Roghayeh Tahernejade and Iran Sheikhshoaie*

Department of Chemistry, Shahid Bahonar University, Kerman, Iran

*Corresponding Author, Tel.&Fax: +9834333257433

E-Mail: i_shoaie@yahoo.com

Received: 8 July 2017 / Received in revised form: 7 August 2017 / Accepted: 12 August 2017 / Published online: 30 September 2017

Abstract- An electrochemical amplified sensor based on carbon paste electrode modified with reduced graphene oxide/NiO nanocomposite (CPE/rGO/NiO-NC) was suggested for kojic acid determination in food samples. rGO/NiO-NC were characterized by SEM and EDAX methods. The CPE/rGO/NiO-NC showed highly catalytic activity to kojic acid electro-oxidation in aqueous solution. The oxidation currents of kojic acid increased linearly with kojic acid concentration by differential pulse voltammetric (DPV) method in the ranges of 0.3–700 μM with limit of detection ~0.09 μM. The ability of CPE/rGO/NiO-NC was check for the analysis of kojic acid in foodstuff.

Keywords- Kojic acid, Reduced graphene oxide/NiO nanocomposite, Electrochemical sensor, Carbon paste electrode

1. INTRODUCTION

Antioxidants are major additive in food samples for preventing diseases. Also, there are many free radicals in human body that presence of antioxidants can be helped to prevent of their damaging effects. There are many antioxidants in food products that kojic acid is useful of them especially in seafood. Kojic acid in combination with quercetin show good anticancer activity for colon cancer [1]. On the other hand, kojic acid show good antibacterial activity and suggested as a skin lightening agent. So, determination of kojic acid is very important due to its side effect. Some analytical method suggested for determination of kojic acid such

as HPLC, spectroscopy and electrochemical methods [2-4]. Electrochemical sensor can be useful compare to other analytical methods due to fast response and highly sensitivity [5-10]. On the other hand, ability of electrochemical sensor for modification helps to them for increasing in sensitivity of analysis [11-20].

Nanomaterials and especially nanocomposite showed different properties compare to other size materials such as good electrical conductivity [21-25]. In between graphene nanosheet with high surface area can be useful as a conductive mediator in modification of electrochemical sensors [26]. Application of conductive nano-materials can be increased sensitivity of electrochemical sensor in drug and food sample analysis [27-34].

Therefore, in the presence study and due to important of kojic acid analysis in food samples, we fabricated a highly sensitive and good selective electroanalytical sensor for kojic acid analysis in food samples. The presence sensor was fabricated by modification of carbon paste electrode with rGO/NiO-NC. The CPE/rGO/NiO-NC showed good ability for analysis of kojic acid in rice win, bean paste and vinegar samples. The fast response, good selectivity and highly sensitivity are main advantage of CPE/rGO/NiO-NC as a kojic acid sensor.

2. EXPERIMENTAL

2.1. Materials and instruments

We use an Autolab, potentiostat/galvanostat for all of the voltammetric study. The CPE/rGO/NiO-NC, Ag/AgCl/KCl and Pt wire were used a working, reference and counter electrodes. A KYKY-EM3200 digital scanning electron microscope was used for morphological investigation. All of the chemicals reagent such as kojic acid, phosphoric acid, nickel nitrate were of A.R. grade and were used as unless otherwise stated from Sigma-Aldrich.

2.2. Preparation of CPE/rGO/NiO-NC

CPE/rGO/NiO-NC was prepared by mixing of 0.1 g of rGO/NiO-NC and graphite powder in the presence suitable amount of graphite powder. Then previous sample was mixed well for 50 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare CPE/rGO/NiO-NC.

2.3. Preparation of real samples

The rice win, bean paste and vinegar samples were prepared according to our previous reported published paper and standard addition method was used for real sample analysis [4].

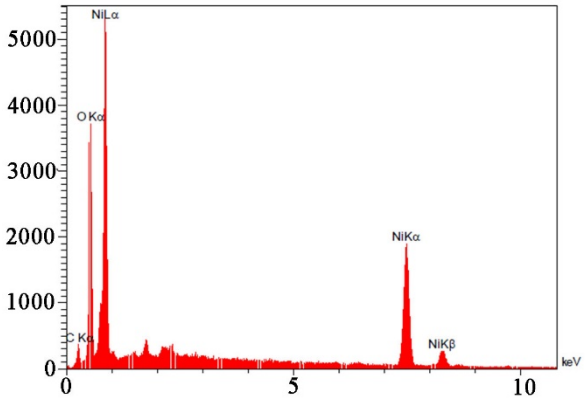
2.4. Synthesis procedure of rGO/NiO-NC

The 1.0 g graphene nanosheet disperses in 50 mL sodium hydroxide (1.0 M). The 50.0 mL nickel nitrate 0.5 M was added to sodium hydroxide solution. The dark sediment filtered and dry at 100 ˚C for 12 h ad then calcined at 450 ˚C for 1.5 hours.

3. RESULTS AND DISCUSSION

3.1. rGO/NiO-NC characterization

The synthesized nano-powder was characterized with EDAX analysis and the obtianed results are presence in Figure 1. As can be seen, the presence of C, O and Ni elements confirms rGO/NiO. The SEM image of rGO/NiO showed spherical shape NiO nanoparticle at a surface of r-GO nanosheet (Figure 2).



Quantitative Results

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg
C	Ka	23.1	62.0639	0.0376	0.0260	10.42	21.95	0.2501		0.00	58.62
O	Ka	315.6	91.8569	0.2561	0.1773	34.26	54.20	0.5175		0.00	344.81
Ni	Ka	320.6	4.9269	0.7063	0.4889	55.33	23.85	0.8837		0.00	58.12
				1.0000	0.6922	100.00	100.00			0.00	

Fig. 1. EDX analysis data for rGO/NiO-NC synthesized in this work

3.2. Voltammetric investigation

The effect of pH was investigated on oxidation current and oxidation potential kojic acid. For this goal the cyclic voltammograms 300 μM kojic acid recorded in the pH 5.0 to 8.0 (Not shown).

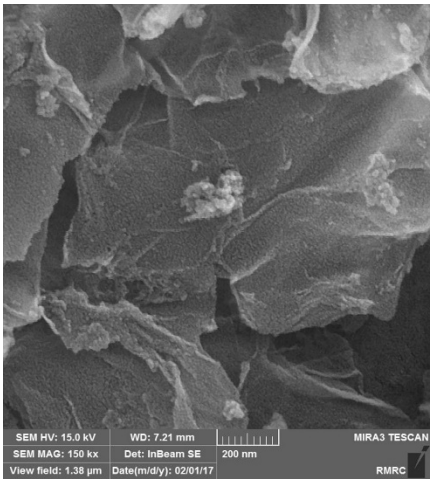


Fig. 2. SEM image of rGO/NiO-NC synthesized in this work

A linear shift of oxidation peak potential towards negative potential with an increasing pH can be obtained and obeyed the regression equation of E_{pa} (V)=-0.0517 pH+1.2533 (R^2=0.9902), which indicates that protons are directly involved in the oxidation of kojic acid (Figure 3).

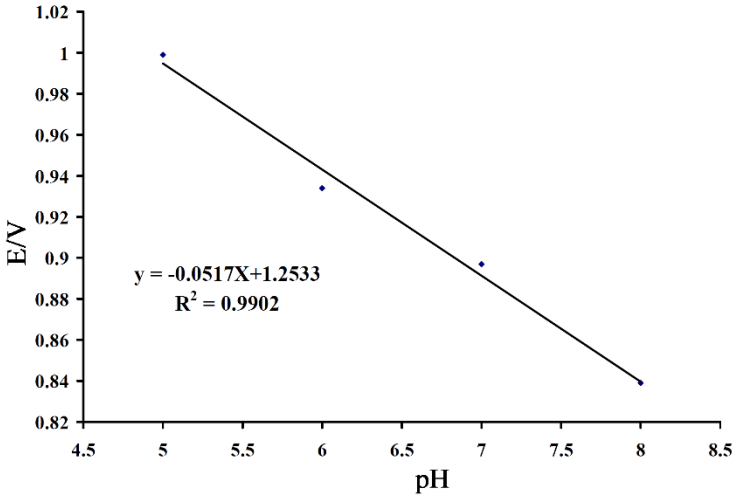


Fig. 3. The relation between oxidation peak potential and pH for electro-oxidation of 300 µM kojic acid

Also, maximum oxidation current was observed at pH=7.0 that was selected as a best condition for next experimental (Figure 4)

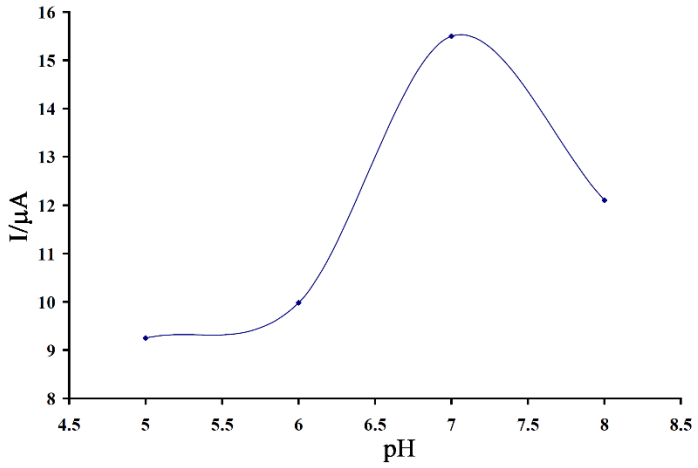


Fig. 4. The relation between oxidation peak current and pH for electro-oxidation of 300 μM kojic acid

The catalytic activity of CPE/rGO/NiO-NC was check by recording cyclic voltammograms of 500 μM kojic acid at a surface of CPE/rGO/NiO-NC (Figure 5 curve a) and CPE (Figure 5 curve b). As can be seen, the oxidation peak current increased from 5.9 μA for CPE to 28.9 μA for CPE/rGO/NiO-NC in the same condition that confirms good electrical conductivity of rGO/NiO-NC. The current density derived from the cyclic voltammograms of 500 μM kojic acid at different electrodes shows in Figure 5 insert. The results show that the presence of rGO/NiO-NC causes the increase of the electrode.

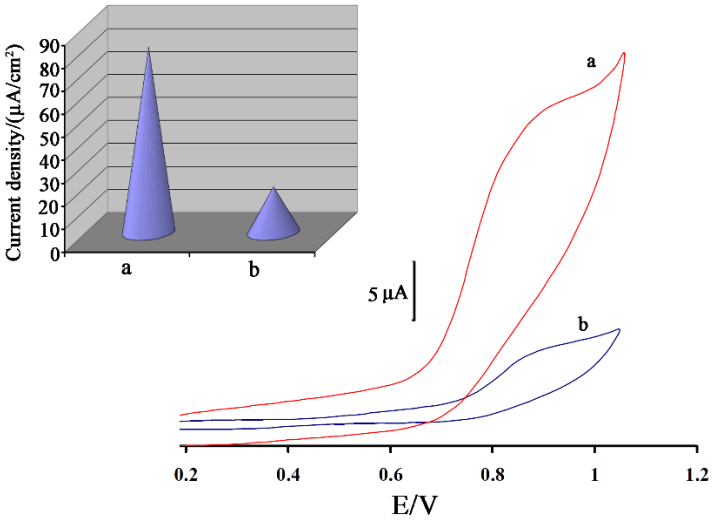


Fig. 5. Cyclic voltammograms of (a) CPE/rGO/NiO-NC and (b) CPE in the buffer solution pH=7.0 in the presence of 500 μM kojic acid. Inset: the current density derived from cyclic voltammogram responses

The effect of scan rate (υ) on the oxidation current of kojic acid C was also examined (Figure 6 inset). The results showed a relation between peak current and $v^{1/2}$ that confirm a diffusion process for oxidation of kojic acid.

Chronoamperometric measurements of kojic acid were recorded at a surface of CPE/rGO/NiO-NC (Figure 7 A). For kojic acid with a diffusion coefficient of D, the Cottrell plot was recorded in figure 7B. From the resulting slope and Cottrell equation the mean value of the D was found to be 1.0×10^{-5} cm^2/s.

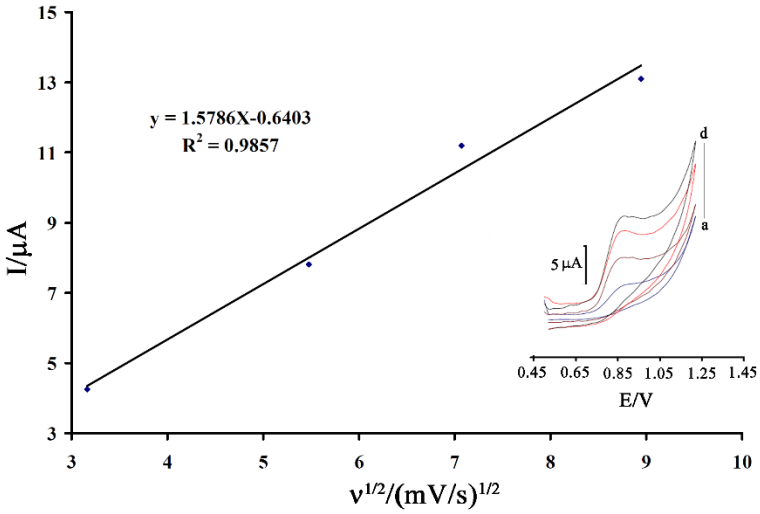


Fig. 6. Variation of anodic peak current *vs.* $v^{1/2}$ for electro-oxidation of 300 µM kojic acid Insert cyclic voltammograms of CPE/rGO/NiO-NC containing 300 µM kojic acid at various scan rates; a-d correspond to 10.0, 30.0, 50.0 and 80.0 mV s^{-1}, respectively

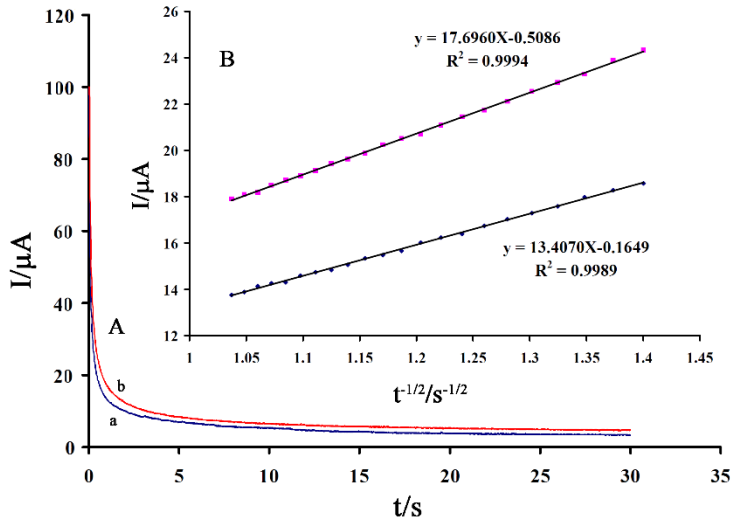


Fig. 7. A) Chronoamperograms obtained at the CPE/rGO/NiO-NC in the presence of (a) 200 and (b) 400 µM kojic acid at pH 7.0. B) Plots of I *vs.* $t^{-1/2}$ obtained from chronoamperograms

3.2. Analysis of kojic acid

Using differential pulse voltammetry (DPV) method, we detect linear dynamic range between 0.3–700 μM for kojic acid at a surface of CPE/rGO/NiO-NC (Figure 8). The detection limit was determined at 0.09 μM.

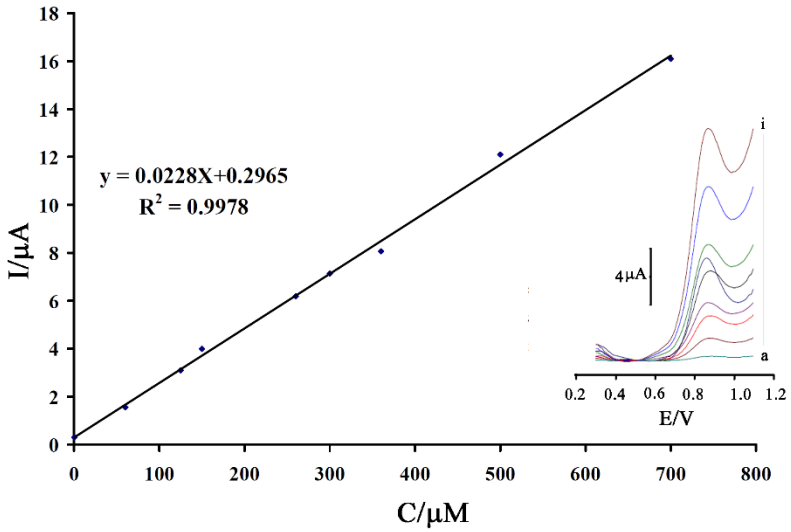


Fig. 8. The plot of oxidation peak current *vs*. kojic acid concentration in the concentration range 0.3-700 μM

3.4. Interference study

In continuous we check selectivity of CPE/rGO/NiO-NC for analysis of 50.0 μM kojic acid with acceptable error <5%. The results indicated that the 100-fold of glucose and glycine, and 700-fold of Li^+, Cl^-, and 200 fold of uric acid did not effect on kojic acid signal.

Table 1. Determination results of kojic acid in real food samples (n=3)

Sample	**Added (μM)**	**Found (μM)**	**Published method (μM)**	**$F_{table\ (98\%)}$**	**$F_{exp.}$**	**$t_{table\ (95\%)}$**	**t_{exp}**
Rice wine	---	15.46±0.53	14.98±0.67	19.0	---	3.8	---
	10.00	25.65±0.76	25.48±0.87	19.0	9.3	3.8	1.9
Bean paste	---	28.45±0.87	29.01±0.97	19.0	---	3.8	---
	20.00	49.03±1.01	48.97±1.22	19.0	13.3	3.8	3.2
Vinegar	---	71.44±0.89	70.89±1.15	19.0	---	3.8	---

3.5. Real sample analysis

We check ability of CPE/rGO/NiO-NC for analysis kojic acid in food samples by standard addition method and data was compared with a published method too [4] (Table 1). The results confirm ability of CPE/rGO/NiO-NC for analysis kojic acid in real samples

4. CONCLUSIONS

In this study, we describe synthesis rGO/NiO-NC by chemical precipitation method and characterized SEM and EDAX methods. In continuous, rGO/NiO-NC was used for modification of carbon paste electrode. The CPE/rGO/NiO-NC was used for analysis of kojic acid in the concentration range 0.3-700 μM. The CPE/rGO/NiO-NC showed good ability for analysis of kojic acid in food samples

REFERENCES

[1] M. Veverka, T. Dubaj, J. Gallovič, V. Jorík, E. Veverková, M. Danihelová, and P. Šimon, Monatshefte für Chemie-Chemical Monthly 146 (2015) 99.
[2] Y. Shih, J. AOAC Int. 84 (2001) 1045.
[3] M. S. Piantavini, D. P. Stremel, Â. C. L. B. Trindade, and R. Pontarolo, Latin Am. J. Pharm. 29 (2010) 1468.
[4] M. Sheikhshoaie, I. Sheikhshoaie, and M. Ranjbar, J. Mol. Liq. 231 (2017) 597.
[5] V. K. Gupta, H. Mahmoody, F. Karimi, S. Agarwal, and M. Abbasghorbani, Int. J. Electrochem. Sci. 12 (2017) 248.
[6] V. Arabali, M. Ebrahimi, S. Gheibi, F. Khaleghi, M. Bijad, A. Rudbaraki, M. Abbasghorbani, and M. R. Ganjali, Food Anal. Methods 9 (2016) 1763.
[7] A. Pahlavan, N. Rezanejad, H. Karimi-Maleh, M. R. Jamali, M. Abbasghorbani, H. Beitollahi, and N. Atar, Int. J. Electrochem. Sci 10 (2015) 3644.
[8] M. Ganjali, P. Norouzi, M. Ghorbani, and A. Ahmadi, Canadian J. Anal. Sci. Spectro. 51 (2006) 244.
[9] S. Salmanpour, M. Abbasghorbani, F. Karimi, R. Bavandpour, and Y. Wen, Current Anal. Chem. 13 (2017) 40.
[10] F. Khaleghi, A. Elyasi Irai, V. K. Gupta, S. Agarwal, M. Bijad, and M. Abbasghorbani, J. Mol. Liq. 223 (2016) 431.
[11] A. A. Ensafi, B. Rezaei, M. Amini, and E. Heydari-Bafrooei, Talanta 88 (2012) 244.
[12] A. A. Ensafi, M. Taei, and T. Khayamian, Int. J. Electrochem. Sci. 5 (2010) 116.
[13] A. A. Ensafi, and R. Hajian, Electroanalysis 18 (2006) 579.
[14] A. A. Ensafi, M. Taei, H. R. Rahmani, and T. Khayamian, Electrochim. Acta 56 (2011) 8176.

[15] A. A. Ensafi, M. Taei, and T. Khayamian, Coll. Surfaces B 79 (2010) 480.
[16] A. A. Ensafi, E. Heydari-Bafrooei, and M. Amini, Biosens. Bioelectron. 31 (2012) 376
[17] M. A. Khalilzadeh, H. Karimi-Maleh, A. Amiri, and F. Gholami, Chin. Chem. Lett. 21 (2010) 1467.
[18] V. K. Gupta, H. Karimi-Maleh, and R. Sadegh, Int. J. Electrochem. Sci. 10 (2015) 303.
[19] A. A. Ensafi, and H. Karimi-Maleh, Int. J. Electrochem. Sci. 5 (2010) 392.
[20] B. J. Sanghavi, and A. K. Srivastava, Electrochim. Acta 55 (2010) 8638.
[21] B. J. Sanghavi, and A. K. Srivastava, Electrochim. Acta 56 (2011) 4188.
[22] N. F. Atta, M. F. El-Kady, and A. Galal, Sens. Actuators B141 (2009) 566.
[23] Y. Xu, X. Ye, L. Yang, P. He, and Y. Fang, Electroanalysis 18 (2006) 1471.
[24] J. B. Raoof, R. Ojani, H. Karimi-Maleh, M. R. Hajmohamadi, and P. Biparva, Anal. Methods 3 (2011) 2637.
[25] Y. Wang, D. Zhang, and J. Wu, J. Electroanal. Chem. 664 (2012) 111.
[26] L. C. Figueiredo-Filho, D. A. Brownson, O. Fatibello-Filho, and C. E. Banks, Analyst 138 (2013) 4436.
[27] A. A Ensafi, H. Karimi-Maleh, and S. Mallakpour, Electroanalysis 23 (2011) 1478.
[28] A. A. Ensafi, H. Karimi-Maleh, and S. Mallakpour, Colloids and Surfaces B 104 (2013) 186.
[29] A. A. Ensafi, H. Karimi-Maleh, and S. Mallakpour, Electroanalysis 24 (2012) 666.
[30] A. Rudbaraki, and M. A. Khalilzadeh, Anal. Bioanal. Electrochem. 8 (2016) 741.
[31] S. Gheibi, G. Gharibi, M. A. Khalilzadeh, and A. Pourfarzad, Anal. Bioanal. Electrochem., 9 (2017) 365.
[32] M. Baghayeri, H. Veisi, H. Veisi, B. Maleki, and H. Karimi-Maleh, H. Beitollahi, RSC Adv. 4 (2014) 49595.
[33] M. Fouladgar, and H. Karimi-Maleh, Ionics 8 (2013) 1163
[34] A. A. Ensafi, and H. Karimi-Maleh, Int. J. Electrochem. Sci. 5 (2010) 1484.