Short Communication

NiO nanoparticle/1-hexyl-3-methylimidazolium hexafluorophosphate composite for amplification of epinephrine electrochemical sensor

Soheila Saghiri, Mahmoud Ebrahimi*, Mohammad Reza Bozorgmehr

Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

ARTICLE INFORMATION

Received: 28 July 2020

Received in revised: 15 October 2020

Accepted: 31 October 2020

Available online: 12 December 2020

DOI: 10.26655/AJNANOMAT.2021.1.4

KEYWORDS

Epinephrine

NiO nanoparticle

1-hexyl-3-methylimidazolium

hexafluorophosphate

Modified sensor

ABSTRACT

In this research study, NiO nanoparticle (NiO-NPs) was synthesis using a simple strategy method (chemical precipitation), then it was utilized for amplification of paste electrode (PE) at the presence of paraffin oil and 1-hexyl-3-methylimidazolium hexafluorophosphate (HPF6). NiO nanoparticle was characterized using the transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) method. The NiO-NPs/HPF6/PE was used as electrochemical sensor for determination of epinephrine in pharmaceutical and urine samples. The sensor improved the oxidation signal of epinephrine about 2.87 times. The pH investigation confirmed that the electro-oxidation of epinephrine was relative to pH changing in the presence two electrons and two protons. The square wave voltammetric investigation showed that the oxidation current of epinephrine has linear relation with its concentration in the range 1.0 nM-300 μ M with detection limit 0.5 nM.

© 2021 by SPC (Sami Publishing Company), Asian Journal of Nanoscience and Materials, Reproduction is permitted for noncommercial purposes.

Graphical Abstract

Introduction

Measuring medicinal compounds from different angles is necessary for the health of the body [1–3]. On the other hand, it is very important to determine the correct dose of drugs using analytical methods [4–14]. Among the various analytical methods such as chromatography, spectroscopy and electrochemistry that have been proposed for the measurement of drug compounds, electrochemical methods have been used more in recent years than other methods [15–23]. Electrochemical techniques have attracted more attention from companies due to their high analysis speed than other methods [24–26].

Epinephrine is a catecholamine drug with unique properties that shows a lot of biological activity in the body [27]. Epinephrine or adrenaline plays an important role in the fight-or-flight response by pupil dilation response, output of the heart, increasing blood flow to muscles, and blood sugar level [28]. Determination of epinephrine in human body is very important to study human healthy [29, 30]. Nanomaterials, especially metal nanoparticles, have revolutionized many scientific fields [31]. Changing the properties of metals by moving towards nanostructures has caused metal nanoparticles to show interesting properties [32, 33]. Nickel oxide nanoparticles are one of the most widely used metal nanoparticles that have high electrical conductivity and are used in the manufacture of electrochemical sensors [34]. The present study describes a simple strategy for synthesis of NiO nanoparticle as conductive mediator. In continuous, the NiO-NPs/HPF6/PE was fabricated using the synthesized NiO nanoparticle and then used as an electrochemical sensor for determination of epinephrine in pharmaceutical samples.

Experimental

Materials and methods

Epinephrine (95%), nickel(II) nitrate hexahydrate, graphite powder, 1-hexyl-3-methylimidazolium hexafluorophosphate, paraffin oil, sodium hydroxide were purchased from the Sigma and Merck companies. Potentiostat/Galvanostat machine (Ivium-Vertex) was used for I-V investigations.

Synthesis of NiO-NPs

100 mL nickel(II) nitrate hexahydrate (0.5 M) was prepared and stirred for 30 min at 35 °C. In continuous, 100 mL sodium hydroxide (1.0 M) was added in nickel salt solution and stirred was continuous for 20 min at same temperature. The precipitated sample was washed five times and dried at 100 °C for 13 h. The green powder was calcinated at 350 °C for 4 h.

Preparation of NiO-NPs/HPF6/PE sensor

To fabricate the NiO-NPs/HPF6, 0.95 g graphite powder+0.5 g NiO-NPs was dispersed into 10 mL methanol. After evaporation of ethanol, suitable amount of paraffin oil+HPF6 was added for converting of powder to paste.

Real sample preparation

Injection and dextrose saline were purchased from local pharmacy and diluted by phosphate buffer solution (pH=7.0) and used for real sample analysis

Results and Discussion

NiO-NPs characterization

TEM image of NiO-NPs is demonstrated in [Figure 1a](#). Results confirmed that the NiO-NPs were successfully synthesized by chemical precipitation method with spherical shape. EDS analysis data confirmed the presence of the Ni

and O elements, showing the purity of the synthesized nano-powder.

Figure 1. a) TEM image of NiO nanoparticle. b) EDS analysis of NiO nanoparticle

Electrochemical behavior of epinephrine

SW voltammograms of epinephrine was recorded at the pH range of 5-9. As can be seen,

the maximum oxidation current of the epinephrine was recorded at pH=7.0 and this pH was selected as optimum condition (Figure 2). In addition, the potential-pH curve of epinephrine showed a slope of 57.1 mV/pH that confirmed two electron and two proton are presence in redox reaction of this compound (Scheme 1).

SW voltammogram of 100 μ M epinephrine was recorded at the surface of PE (Figure 3, curve a), NiO-NPs/PE (Figure 3, curve b), HPF6/PE (Figure 3 curve c) and NiO-NPs/HPF6 (Figure 3 curve d), respectively. With moving of PE to NiO-NPs/HPF6/PE oxidation current of epinephrine was improve from 7.18 μ A to 20.6 μ A that confirm high conductivity of two mediators.

Linear sweep voltammogram of epinephrine was recorded at the surface of the NiO-NPs/HPF6/PE at optimum condition (Figure 4). Linear relation between the current and $v^{1/2}$ was observed for the epinephrine in this study, confirming the diffusion process for the redox reaction of drug at surface of NiO-NPs/HPF6/PE.

Figure 2. Ep-pH curve for electro-oxidation of 100 μ M epinephrine. Inset) Relative SW voltammograms for electro-oxidation of 100 μ M epinephrine

Scheme 1. Electro-oxidation mechanism of epinephrine

Figure 3. SW voltammogram of 100 μM epinephrine at surface of a) PE, b) NiO-NPs/PE, c) HPF6/PE and d) NiO-NPs/HPF6

Figure 4. $I-v^{1/2}$ curve for electro-oxidation of 500 μM epinephrine. Linear sweep voltammogram of 500 μM epinephrine at scan rate a) 10, b) 30, c) 60 and d) 120 mV/s

SW voltammograms of epinephrine was recorded in the concentration range 1.0 nM-300 μM at surface of NiO-NPs/HPF6/PE (Figure 5). Results showed a linear relation between

oxidation current of epinephrine and its concentration in the range 1.0 nM–300 μ M with detection limit 0.5 nM (Figure 5).

Selectivity of NiO-NPs/HPF6/PE as new analytical sensor for determination of epinephrine was assessed in this step. The results revealed that the NiO-NPs/HPF6/PE has good selectivity for determination of 5.0 μ M epinephrine at the presence of folic acid,

methionine, valine, Li^+ , Cl^- , Mg^{2+} , phenylalanine and glucose. In the final step, the NiO-NPs/HPF6/PE was used to determine the epinephrine in the injection and dextrose saline samples using the standard addition method. The results are shown in Table 1, confirming the high ability of the NiO-NPs/HPF6/PE for determination of the epinephrine in real samples.

Figure 5. I-C curve for electro-oxidation of epinephrine in concentration range 1.0 nM–300 μ M. SW voltammograms of epinephrine in concentration range 1.0 nM–300 μ M

Table 1. Determination of epinephrine in real sample

Sample	Added (μ M)	Expected (μ M)	Founded (μ M)	Recovery %
Injection	---	2.00	2.11 $\pm$ 0.34	105.5
	10.00	12.00	12.56 $\pm$ 0.78	104.66
	20.00	20.00	19.87 $\pm$ 0.95	99.35
Dextrose Saline	---	---	<LOD	--
	5.00	5.00	4.87 $\pm$ 0.34	97.4

Conclusions

The presence study suggested a simple strategy for the synthesis of the NiO-NPs. The synthesized NiO-NPs demonstrated a good catalytically activity for the fabrication of the epinephrine electrochemical sensor. The NiO-NPs/HPF6/PE showed a linear dynamic range

1.0 nM–300 μ M with the detection limit of 0.5 nM for determination of the epinephrine in aqueous solution. Finally, the NiO-NPs/HPF6/PE was used to determine the epinephrine in injection and dextrose saline samples with acceptable recovery data. The square wave voltammetric investigation revealed that the oxidation current of

epinephrine has linear relation with its concentration in the range 1.0 nM-300 µM with the detection limit of 0.5 nM.

Disclosure Statement

No potential conflict of interest was reported by the authors.

References

- [1]. Baghayeri M., Rouhi M., Lakouraj M.M., Amiri-Aref M. *J. Electroanal. Chem.*, 2017, **784**:69
- [2]. Baghayeri M., Alinezhad H., Fayazi M., Tarahomi M., Ghanei-Motlagh R., Maleki B. *Electrochim. Acta.*, 2019, **312**:80
- [3]. Baghayeri M., Ansari R., Nodehi M., Razavipanah I., Veisi H. *Microchim. Acta*, 2018, **185**:320
- [4]. Ghanei-Motlagh M., Baghayeri M., J. *Electrochem. Soc.*, 2020, **167**:066508
- [5]. Nodehi M., Baghayeri M., Ansari R., Veisi H., *Mater. Chem. Phys.*, 2020, **244**:122687
- [6]. Baghayeri M., Ghanei-Motlagh M., Tayebee R., Fayazi M., Narenji F., *Anal. Chim. Acta.*, 2020, **1099**:60
- [7]. Baghayeri M., Nodehi M., Veisi H., Tehrani M.B., Maleki B., Mehmandost M, *Drug J. Pharm. Sci.*, 2019, **27**:593
- [8]. Baghayeri M., Alinezhad H., Tarahomi M., Fayazi M., Ghanei-Motlagh M., Maleki B., *Appl. Surf. Sci.*, 2019, **478**:87
- [9]. Baghayeri M., Ansari R., Nodehi M., Razavipanah I., Veisi H., *Electroanalysis*, 2018, **30**:2160
- [10]. Brenner D., Mahbooba Z., Saberi-Movahed F., Krim J., Liu Z., Ivanov M.G., Osawa E., Shenderova O. *Mater. Res. Soc. Symp. Proc.*, 2014, 1703 DOI: 10.1557/opl.2014.840
- [11]. Raoof J.B., Ojani R., Baghayeri M., *Sens. Actuators B*, 2019, **143**:261
- [12]. Saberi Movahed F., Cheng G.C., Venkatachari B.S., Cozmuta I. *42nd AIAA Thermophysics Conference 27-30 June 2011, Honolulu, Hawaii*
- [13]. Baghayeri M., Nazarzadeh Zare E., Mansour Lakouraj M., *Biosens. Bioelectron.*, 2014, **55**:259
- [14]. Karimi F., Zakariae N., Esmaeili R., Alizadeh M., Tamadon A.M., *Curr. Biochem. Eng.*, 2020, **6**:114
- [15]. Baghayeri M., Veisi H., Ghanei-Motlagh M., *Sens. Actuators B*, 2017, **249**:321
- [16]. Baghayeri M., Zare E.N., Namadchian M., *Sens. Actuators B*, 2013, **188**:227
- [17]. Baghayeri M., Namadchian M., *Electrochim. Acta*, 2013, **108**:22
- [18]. Baghayeri M., Zare E.N., Lakouraj M.M., *Microchim. Acta*, 2015, **182**:771
- [19]. Baghayeri M., Ansari R., Nodehi M., Razavipanah I., Veisi H., *Microchim. Acta*, 2018, **185**:320
- [20]. Baghayeri M., *Rsc Adv.*, 2015, **5**:18267
- [21]. Baghayeri M., Rouhi M., Lakouraj M.M., Amiri-Aref M., *J. Electroanal. Chem.*, 2017, **784**:69
- [22]. Raoof J.B., Ojani R., Baghayeri M., *Chin. J. Catal.*, 2011, **2**:1685-1692
- [23]. Raoof J.B., Ojani R., Baghayeri M., *Anal. Methods*, 2011, **3**:2367
- [24]. Bavandpour R., Rajabi M., Karimi-Maleh H. *New J. Chem.*, 2020, **44**:11125
- [25]. Baghayeri M., Alinezhad H., Fayazi M., Tarahomi M., Ghanei-Motlagh R., Maleki B. *Electrochim. Acta.*, 2019, **312**:80
- [26]. Golikand A.N., Raoof J., Baghayeri M., Asgari M., Irannejad L. *Russ. J. Electrochem.*, 2009, **45**:192
- [27]. Gueugniaud P.-Y., David J.-S., Chanzy E., Hubert H., Dubien P.-Y., Mauriau-court P., Bragança C., Billères X., Clotteau-Lambert M.-P., Fuster P., *N. Engl. J. Med.*, 2008, **359**:21
- [28]. Deibert D.C., Defronzo R.A., *J. Clin. Investig.*, 1980, **65**:717
- [29]. Kharian S., Teymoori N., Khalilzadeh M.A., *J Solid State Electrochem.*, 2012, **16**:563

- [30]. Sadeghi R., Karimi-Maleh H., Bahari A., Taghavi M., *Phys. Chem. Liq.*, 2013, **51**:704
- [31]. Malekmohammadi S., Hadadzadeh H., Farrokhpour H., Amirghofran Z. *Soft Matter.*, 2018, **14**:2400
- [32]. Malekmohammadi S., Hadadzadeh H., Rezakhani S., Amirghofran Z. *ACS Biomater. Sci. Eng.*, 2019, **5**:4405
- [33]. Malekmohammadi S., Hadadzadeh H., Amirghofran Z. *J. Mol. Liq.*, 2018, **265**:797
- [34]. Alizadeh M., Azar P., Mozaffari S., Karimi-Maleh H., Tamaddon A., *Front. Chem.* 2020, **8**:677

How to cite this manuscript: Soheila Saghiri, Mahmoud Ebrahimi*, Mohammad Reza Bozorgmehr. NiO nanoparticle/1-hexyl-3-methylimidazolium hexafluorophosphate composite for amplification of epinephrine electrochemical sensor. *Asian Journal of Nanoscience and Materials*, 4(1) 2021, 46-52. DOI: 10.26655/AJNANOMAT.2021.1.4