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ORIGINAL PAPER

Sensitive amperometric detection of omeprazole and pantoperazole at electrodeposited nickel oxide nanoparticles modified glassy carbon electrode

Abdollah Salimi · Zahra Enferadi · Abdollah Noorbakhash · Kayomars Rashidi

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Abstract Glassy carbon electrode modified with electrodeposited nickel oxide nanoparticles (NiOxNPs) was used as electrocatalyst for oxidation of omeprazole and pentoperazole in alkaline solution. The modified electrode exhibited efficient electrocatalytic activity for the oxidation of omeprazole and pentoperazole with relatively high sensitivity, excellent stability, and long lifetime. Hydrodynamic amperometric method is used for determination of selected analytes. Under optimized condition, the linear concentration range, detection limit, and sensitivity of modified electrode toward omeprazole detection are 4.5–120 μM, 0.4 μM (at signal to noise 3), and 40.1 nA μM^{-1} cm^{-2}, respectively. For pantoperazole, hydrodynamic amperometric determination yielded calibration curve with linear range of 2.5–180 μM, detection limit of 0.2 μM, and sensitivity of 39.2 nA μM^{-1} cm^{-2}, respectively. The proposed method was successfully applied to pentoperazole and omeprazole determination in drug samples.

A. Salimi · Z. Enferadi · A. Noorbakhash
Department of Chemistry,
University of Kurdistan,
P.O. Box 416, Sanandaj, Iran

A. Salimi (✉)
Nanotechnology Research Center,
University of Kurdista,
P.O. Box 416, Sanandaj, Iran
e-mail: absalimi@uok.ac.ir

A. Salimi
e-mail: absalimi@yahoo.com

K. Rashidi
Department of Pharmacology,
Kurdistan Medical University,
Sanandaj, Iran

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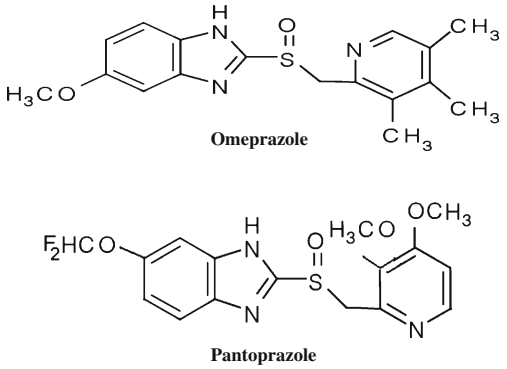
Introduction

Pantoprazole(PNZ)5-(difluoromethyl)-2-[3,4-dimethoxy-2-pyridyl)methylsulfinyl]1H-benziimidazole and omeprazole (OMZ), 5-methoxy-2[[(4-methoxy-3,5-dimethyl-2-pyridinyl) methyl] sulphinyl]-1Hbenzidimazole (Scheme 1) are substituted benzimidazole compounds and they are good proton pump inhibitors which reduce gastric acid secretion [1, 2]. They mainly act to regulate acid production in the stomach and are used for treating various acid-related disorders such as duodental, gastric, and esophageal ulceration [3, 4]. Therefore, determining of these drugs in pharmaceutical formulations and biological samples is very important. Many analytical methods, such as high-performance liquid chromatography (HPLC) [5–12], microdialysis and HPLC [13], HPLC–mass spectrometry [14], HPLC–tandem mass spectrometry [15], HPLC with coulometric detection [16], liquid chromatography–electrospray quadrupole liner ion trap mass spectrometry [17], solid phase extraction and micellar electrokinetic capillary chromatography [18], liquid chromatography with liquid–liquid extraction [19], UV-visible spectrophotometry [20–22], and derivative spectroscopy [23, 24], have been used for quantitative determination of pantoperazole and omoprazole in drug formulations, plasma, and other biological fluids. Although the chromatographic methods have sufficient sensitivity for determination of OMZ and PNZ in pharmaceutical dosage forms and in biological fluids, they require sample pretreatment and time-consuming extraction steps prior to assay of the drugs. Therefore, it is important to develop new methods with less experimental and



Scheme 1 Chemical structures of omeprazole and pantoprazole

instrumental necessity capable for determination of drug concentration in pharmaceutical samples. Electrochemical methods have been proved to be an inexpensive and effectives way for determination of various compounds without derivatization process [25]. As a result, they have been used for determination of a wide range of pharmaceutical formulations. The reduction process and quantitative determination of omeprazole and lansoprazole have been investigated by several polarographic techniques [26–29]. Differential pulse voltammetry and cyclic voltammetry at mercury, carbon paste, and glassy carbon electrodes were used for the determination of lansoprazole, pantoprazole, and omeprazole in pharmaceutical formulations [30–33]. Although electrochemical methods have been proved to be an inexpensive and effective way for omeprazole and pantoperazole determination, direct reduction or oxidation of these drugs at bare electrodes are not suited for analytical application due to slow electrode kinetics and high overpotentials required for redox reactions on many electrodes materials. For this reason, redox mediators have been widely used in order to decrease the overpotential and increase the electron transfer kinetics. Electrochemical sensors and biosensors developed with nanomaterials offers highly sensitive, real-time detection of clinically important analytes with low power requirements for decentralized testing in remote locations [34–37]. Metal oxide particles and nanoparticles such as manganese oxide, nickel oxide, zirconium oxide, titanium oxide, tungsten oxide, iridium oxide, and iron oxide have been successfully used for immobilization and direct electrochemistry of biomolecules [38]. In the past, research on the synthesis of nanosized porous nickel oxide materials and its applications in catalytic reactions, industrial processes and electrochromic devices has been rather intense [39–41]. Furthermore, due to the excellent electrocatalytic activity and good antifouling properties of electrodes modified with nickel oxide, these modified electrodes have been used for electrocatalytic oxidation and determination of insulin, thiols, disulfides, mercaptans, and sulfur oxoanions [42–44]. In this study, due to chemical stability and electrochemical reversibility of Ni(II)/Ni(III) redox couple, glassy carbon electrode modified with nickel oxide nanoparticles was successfully used for oxidation of sulfoxide functional group in omeprazole and pantoperazole to sulphone derivatives. The observed electrocatalytic response of the modified electrode is related to the concentration of selected drugs. To evaluate the possible analytical application of modified electrode, it has been used for voltammetric and amperometric detection of omeprazole and pantoperazole at the micromolar concentration range.

Experimental

Chemicals and reagents

For the purpose of this study, omeprazole, pantoperazole, and $Ni(NO_3)_2.H_2O$ were purchased from Sigma and used without further purification. The phosphate-buffered solutions (0.1 M) were prepared form KH_2PO_4 and K_2HPO_4 and the pH was adjusted with HCl and KOH solutions. All solutions were prepared with double-distilled water. Pure N_2 was passed through the solution to avoid possible oxidation during the experiments. The surface morphology of the modified electrode was characterized with atomic force microscope (AFM) and scanning electron microscopy (SEM) techniques. Electrochemical experiments were performed with a computer controlled μ-Autolab modular electrochemical system (Eco Chemie Ultecht, the Netherlands), driven with GPES software (Eco Chemie). A conventional three-electrode cell was used with an Ag/AgCl(sat. KCl) as reference electrode, Pt wire as counter electrode, and glassy carbon disk as working electrode. All experiments were carried out at ambient temperature of 20±1 °C.

Preparation of nickel oxide-modified glassy carbon electrode

The electrode modification method was reported in our previous report [45]. First, glassy carbon electrode (2 mm diameter) was carefully polished with alumina on polishing cloth and then it was placed in ethanol and sonicated to remove adsorbed particles. The electrodeposition of metallic nickel was carried out using potential cycling (20 scans between 1.0 and −1.0 V at scan rate 50 mVs^{-1}) in pH 4 acetate buffer solution containing 1 mM of nickel nitrate. The potential was repetitively cycled (30 scans) from 1.0 to −1.0 V at scan rate of 100 mVs^{-1} in fresh phosphate solution for electrodissolution and passivation of a nickel oxide layer onto glassy carbon (GC) electrode.

Analysis of omeprazole and pantoperazole in pharmaceutical formulations (tables and capsules)

The nickel oxide nanoparticles modified glassy carbon electrode was used for the determination of omeprazole and pantoperazole in tablets and capsules (Razi Manufacture Co). The average mass of five tablets were determined and finely powdered. Then the sample was transferred to 25 ml buffer solution. The solution was filtered, 1 ml of the filtrate solution was diluted to 5 ml then 100 μl of this dilute sample was transferred to the electrochemical cell containing 5 ml of the buffer solution.

Results and discussion

Formation of nickel oxide film

The formation of nickel oxide layer on the electrode surface was checked by recording the cyclic voltammograms of the modified electrode in alkaline solution (Fig. 1). After nickel dissolution and oxide formation in alkaline solution, the anodic peak at 0.48 V is then observed due to the oxidation of the $Ni(OH)_2$ phase to NiO(OH). The corresponding cathodic peak at 0.41 V represents the reduction of NiO(OH) to $Ni(OH)_2$ [46]. For bare GC electrode, no redox response was observed at potential range 0.0–0.7 V. The formation and growth of the nickel oxide nanoparticles on glassy carbon electrode was also investigated by taking AFM and SEM images (Fig. 2). As shown, nickel oxide particles have grown by electrodeposition on the amorphous glassy carbon surface. The images also show that the nickel oxide nanoparticles with an average diameter ranging from 30 to 50 nm, uniformly electrodeposited on the surface of GC electrode.

The effect of pH on the electrochemical behavior of nickel oxide nanoparticles modified glassy carbon electrode

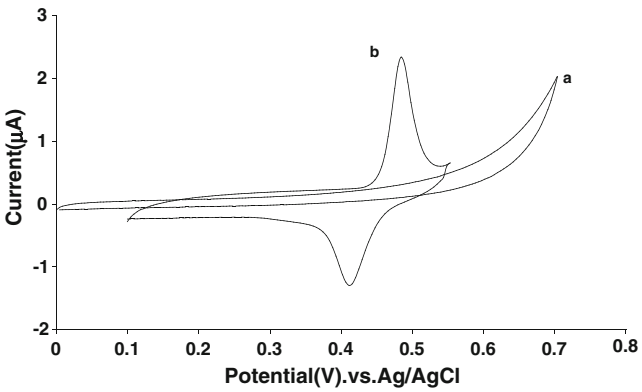


Fig. 1 Cyclic voltammograms of bare GC electrode (*a*) and GC electrode modified with nickel oxide nanoparticles in buffer solution (pH 13) at scan rate 20 mV s^{-1}

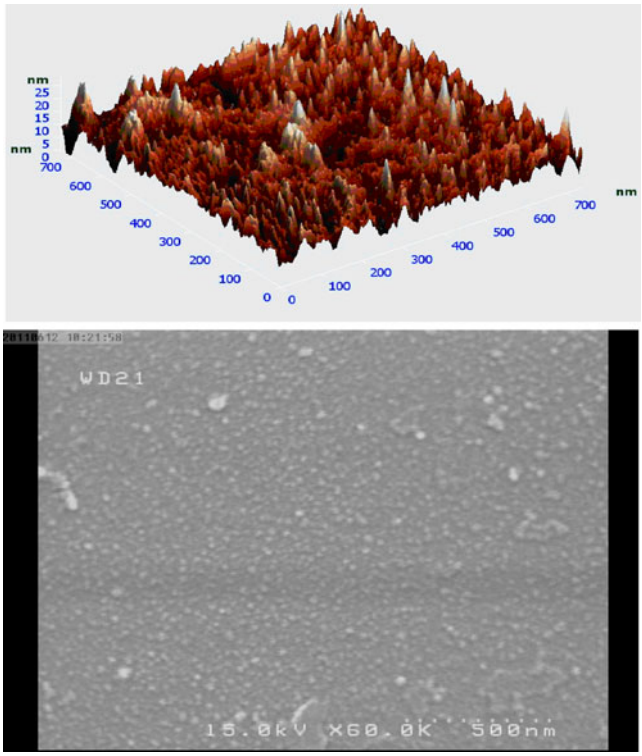


Fig. 2 The AFM (*up*) and SEM (*down*) images of GC electrode modified with electrodeposited nickel oxide nanoparticles

was investigated. The cyclic voltammograms of the modified electrode at different pH solutions were recorded (not shown). Results indicated that the currents, responses are increased with increasing the pH values. At the same time, both reduction and oxidation peak potentials of the β-$Ni(OH)_2$/β-NiOOH redox couple are shifted to less positive values and no peak currents were observed at pH values below 9. This result indicates the redox reaction process coupled with proton transfer which is depicted as follows:

$$\beta - \mathrm{Ni(OH)_2} + \mathrm{OH^-} \rightarrow \beta - \mathrm{NiOOH} + H_2O + \mathrm{e^-} \qquad (1)$$

Electrocatalytic oxidation of OMZ and PNZ at NiOxNP modified electrode

In order to examine the electrocatalytic activity of the modified electrode cyclic voltammograms, bare and modified electrode were recorded in the presence and absence of OMZ and PNZ. Figure 3a, b shows the recorded cyclic voltammograms of modified and bare GC electrode in the absence and presence of OMZ and PNZ in 0.1 M NaOH solution. The enhancement in anodic peak current as well as the decreasing of cathodic peak current appeared by the addition of 5 mM of the proposed drugs indicating a strong catalytic effect. The anodic wave for OMZ and PNZ oxidation starts at 0.45 V and anodic peak potential is about 0.55 V while at the surface of bare glassy carbon

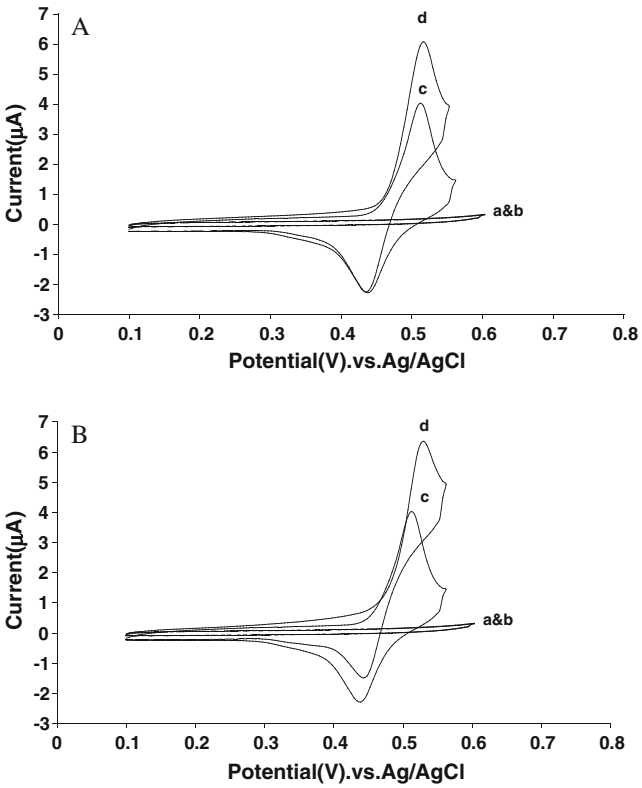


Fig. 3 **a** Cyclic voltammograms of NiOxNPs modified GC electrode in pH 13 solution at scan rate 20 mV s^{-1} in the absence (*c*) and presence 80 μM of pantoparazole (*d*). *a* and *b* as *c* and *d* for bare GC electrode. **b** as **a** in the absence and presence of omeprazole

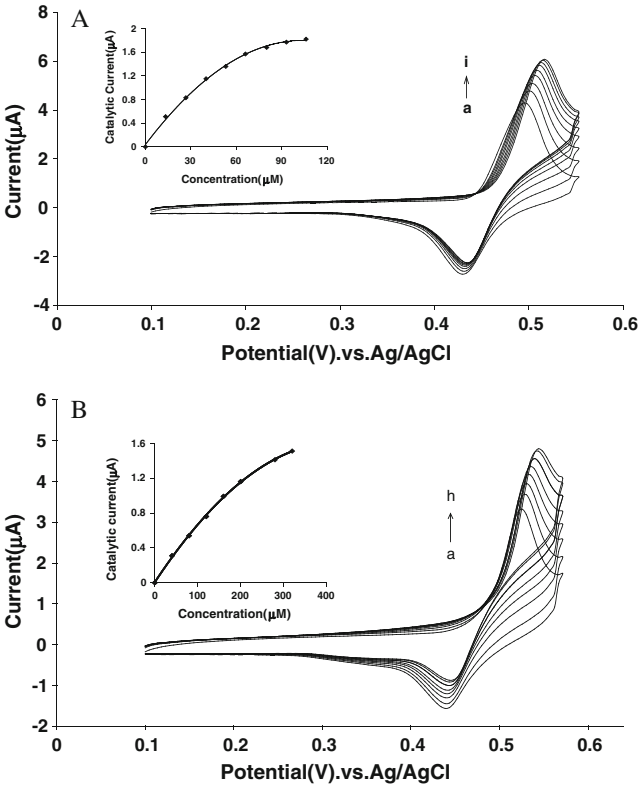


Fig. 5 **a** Cyclic voltammograms of NiOx modified GC electrode at scan rate 20 mVs^{-1} in pH 13 buffer solution containing different concentration of omeprazole (from inner to outer) 0.0, 15, 30, 45, 60, 75, 85, 95, and 105 μM. *Inset* plot of catalytic peak current vs. omeprazole concentrations. **b** Recorded cyclic voltammograms of the modified electrode in the presence different concentration of pantoprazole, from inner to outer, 40, 80, 120, 160, 200, 280, and 320 μM. *Inset* plot of catalytic peak current vs. pantoprazole concentrations

electrode, the proposed analytes were not oxidized at the potential range of 0.0–0.8 V. Thus, decreases in overpotential and enhancement in peak current are achieved in the modified electrodes for OMZ and PNZ oxidation. In order to optimize the electrocatalytic response of modified electrodes toward oxidation of the selected analytes, the effect of pH on the electrocatalytic oxidation behavior of

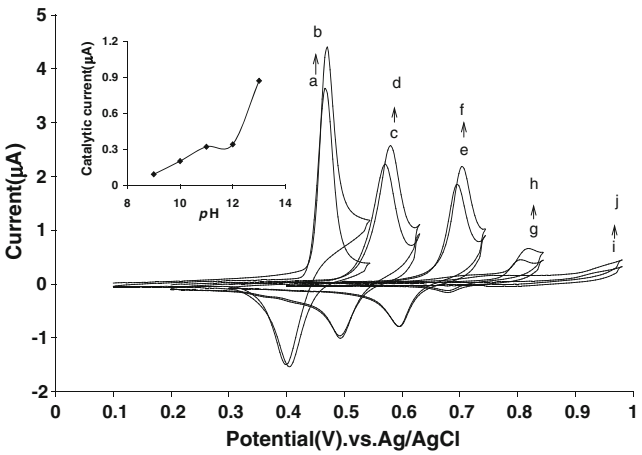


Fig. 4 Recorded cyclic voltammograms of modified electrode in the absence and presence 80 μM of omeprazole at different buffer solutions, from *right* to *left*, 9–13, scan rate 20 mVs^{-1}. *Inset* variation of catalytic peak currents (I_c) vs. pH values

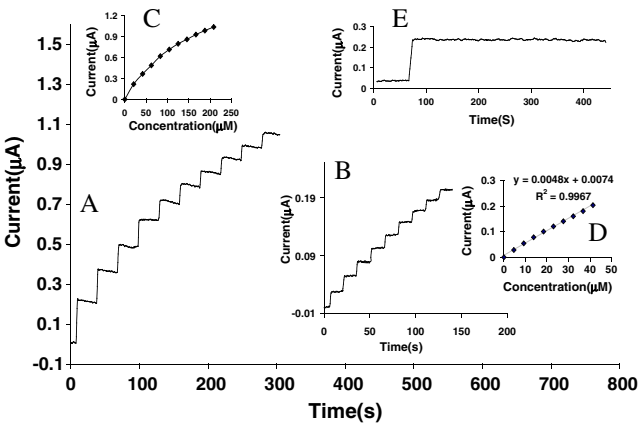


Fig. 6 Amperometric response at rotating NiOx nanoparticles modified GC electrode (rotation speed 2,500 rpm), potential was held at +0.55 V in pH 13 for successive addition of **a** 22 μM and **b** 4.5 μM of omeprazole, **c** and **d** plot of chronoamperometric currents vs. omeprazole concentrations. **e** The recorded chronoamperogram for 40 μM of omeprazole during 500 s

Table 1 Analytical parameters for electrochemical detection of omeprazole and pentoprazole

Electrode	Analyte	Method	Dynamic range	Limit of detection	Sensitivity	Ep (V)
HMDE[a] [47]	Pantoprazol	ACSV[d]	1.0–50 nM	0.5 nM	28.33 nA/nM	1.27
GCE[b] [33]	Pantoprazol	DPAV[e]	6–800 μM	0.4 μM	0.43 μA/μM	1.2
GCE [32]	Omeprazole	DPV[f]	2.9–58 μM	0.55 μM	–	0.75
HMDE [30]	Omeprazole	DPP[g]	0.4–12 mg l^{-1}	0.145 μM	0.011 μA/μM	−0.15
Carbon paste electrode [31]	Omeprazole	DPV	0.2–50 μM	0.025	0.49 μA/μM	0.9
NiOxNP-GCE [c]	Omeprazole	Amperometry	4.5–120 μM	0.4 μM	40.1 nA μM^{-1} cm^{-2}	0.55
[Present study]	Pantoprazole		2.5–180 μM	0.2 μM	39.21 nA μM^{-1} cm^{-2}	0.55

[a] Hanging mercury drop electrode

[b] Glassy carbon electrode

[c] Nickel oxide nanoparticles modified glassy carbon electrode

[d] Adsorptive cathodic stripping voltammetry

[e] Differential pulse anodic voltammetry

[f] Differential pulse voltammetry

[g] Differential pulse polarography

modified electrode was investigated. The cyclic voltammograms of glassy carbon electrode modified with nickel oxide film in 80 μM OMZ concentration at different pH values (9–13) were recorded (Fig. 4). With increasing pH values, the OMZ oxidation peak potential shifts to a less positive value and the peak current increases. Since more reproducible results and high catalytic activity of modified electrode is observed at pH 13, this pH was selected as optimum value for OMZ determination. The same electrocatalytic behavior for oxidation of PNZ was observed at glassy carbon electrode modified with nickel oxide nanoparticles. In order to evaluate the electrocatalytic activity of modified electrode toward oxidation of OMZ and PNZ, the cyclic voltammograms of the GC/NiOx nanoparticles electrode in the presence of different concentrations of selected analytes were recorded (Fig. 5). As shown, the anodic peak currents increased and cathodic peaks decreased with increasing OMZ and PNZ concentration.

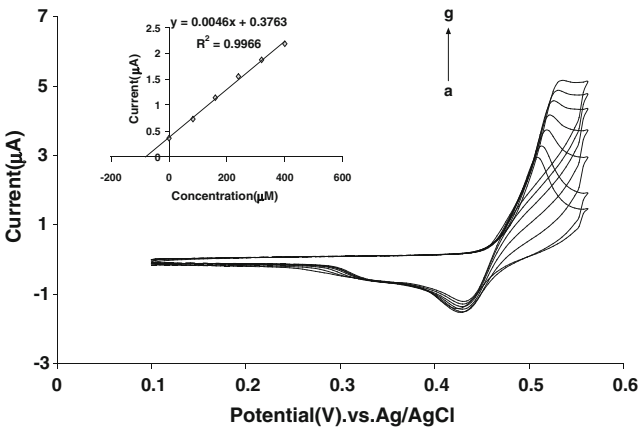


Fig. 7 (*a*) Cyclic voltammograms of modified electrode for omeprazole solution prepared with dissolving omeprazole tablets in pH 13 at scan rate 20 mVs^{-1} (*b–e*) as *a* in the presence different concentration of omeprazole (90, 180, 270, 360, and 450 μM). *Inset* plot of peak current vs. added omeprazole concentration

The fouling of electrode surfaces represents a significant problem in diagnostic systems and as a result, there is a great deal of interest in devising strategies to minimize surface fouling. The antifouling property and stability of electrocatalytic activity of nickel oxide film for oxidation of OMZ and PNZ is examined by repetitive scanning at a scan rate of 20 mV s^{-1} (not shown). In the first five scans, the electrocatalytic currents decreased with scan number and then the current remained at 85% of its initial value after 30 cycles. These results indicate stable activity of the film surface and reflect the remarkably progressive antifouling properties of the film. The reproducibility of the nickel oxide-modified GC electrode for catalytic oxidation of selected drugs was evaluated by five successive electrode modifications. Then cyclic voltammograms of modified electrode were recorded in 80 μM of PNZ solutions (the relative standard deviation (RSD) for five measured anodic peak currents was 4%). The RSD of the peak currents of 80 μM of OMZ for seven repeated determinations is also 3%. Therefore at the modified electrode, not only the overvoltage for OMZ and PNZ oxidation decrease but also the antifouling properties of nickel oxide nanoparticles film improve reproducibility.

In order to obtain more information about the electrocatalytic activity of modified electrode toward oxidation of OMZ and PNZ, 100 μM cyclic voltammograms of OMZ solution at different scan rates were recorded (not shown).

The peak current for the anodic oxidation of OMZ is proportional to the square root of the scan rate suggesting that the process is controlled by diffusion of analytes as expected for a catalytic system. It can also be noted that by increasing the sweep rate, the peak potential for the catalytic oxidation of OMZ shifts to more positive values and plot of peak current vs. square rate of scan rate deviates from linearity (at v>200 mV s^{-1}; not shown) suggesting a kinetic limitation in the reaction between the redox sites of the nickel oxide and OMZ. Based on the results, the following catalytic scheme (*EC′* catalytic mechanism) describes the reaction sequence in the oxidation of OMZ by nickel oxide nanoparticles film:

$$Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^- \quad (2)$$

$$R - SO - R' + 2NiO(OH) + H_2O \rightarrow R - SO_2 - R' + 2Ni(OH)_2 \quad (3)$$

Amperometric detection of OMZ and PNZ at NIOx nanoparticles modified GC electrode. As indicated, GC/NiOx/NPs-modified electrode has excellent and stable electrocatalytic activity toward oxidation of OMZ and PNZ. In order to obtain good repeatability and high sensitivity, the amperometric method at fixed potential was used. Figure 6 displays the typical steady-state catalytic current time response of the rotated modified electrode (2,000 rpm) with successive injection of OMP at an applied potential 0.55 V vs. reference electrode. As illustrated in the figure, a well-defined response was observed during the successive addition of 20 and 4.5 μM of omeprazole. These results demonstrate a stable and efficient catalytic property of the electrocatalyst. There is a linear relation between response current and omeprazole concentration up to 120 μM, while for a higher concentration of omeprazole, the plot of current vs. analyte concentration deviates from linearity (Fig. 6c). The linear least squares calibration curve over the concentration range of 4.5–40.5 μM (nine points) is $I(\mu A)$=0.0048 [omeprazole]μM+0.0074 μA with a correlation coefficient of 0.9967 indicating that the regression line is very well fitted with the experimental data. Therefore, the regression equation can be used for determination of unknown samples. The detection limit (signal to noise of 3) and sensitivity were 0.4 μM, 40.1 nA M^{-1} cm^{-2}, respectively. For pantoprazole, detection limit and sensitivity were 0.2 μM, 39.2 nA μM^{-1} cm^{-2} and concentration range was up to 180 μM. These analytical parameters are comparable and even better than those obtained by using other modified electrodes [26–33]. Figure 6e shows the amperometric response of 40 μM omeprazole during prolonged 500-s experiment. As can be seen, the response remains stable throughout the experiment indicating the antifouling properties of omeprazole and its oxidation products towards the electrode surface. Therefore, the modified electrode has excellent, stable, and strong mediation properties and facilitates the low potential amperometric measurement of omeprazole and pantoprazole. The analytical parameters for the proposed modified electrode presented in the present study are comparable with reported values in literature for detection of omeprazole and pantoperazole based on electroanalytical methods (Table 1).

Analysis of omeprazole and pantoperazole in drug samples

The nickel oxide nanoparticles modified glassy carbon electrode was used for the determination of omeprazole and pantoperazole in tablets and capsules (Razi Manufacture Co). Figure 7 has shown the voltammetric response of solutions containing OMP of tablets and various concentration of OMP (standard additions). The content of OMP in tablets was calculated from interpolation of the curve. The calculated value for OMP in each tablet is 39.3(±0.5) mg which is near to the real value of the OMP in drug samples (40±0.5 mg). The same procedure was applied for pantoperazole analysis in capsules. The content of PNZ in each capsule is obtained 20.3(±0.5)mg which is also close to real value of the PNZ in drug samples (20±0.5 mg). These results indicate that the proposed method has high accuracy and it can be used for routine analysis in drug quality control laboratories.

Conclusion

In conclusion, nickel oxide nanoparticles were grown at the GC electrode through a simple electrodeposition process using cyclic voltammetry. The modified electrode shows excellent electrocatalytic activity towards oxidation of OMP and PNZ at reduced overpotential in alkaline solutions. The results indicate that the modified electrode facilitates determination of OMP and PNZ with good sensitivity and reproducibility compared to similar-based electrodes or other instrumental methods. This sensor can be used for amperometric determination of selected analytes as micromolar or lower concentration range with good reproducibility and little fouling effects of analytes and their oxidation products. The modified electrode has been used for determination of OMP in drug samples. The proposed method offers the advantages of accuracy and time saving as well as simplicity of reagents and apparatus. The proposed modified electrode promised as novel amperometric detector for detection various biomolecules and drug samples using flow injection analysis or liquid chromatography techniques.

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References

1. Langtry HD, Wilde MI (1998) Drugs 56:4447–486
2. Anderson T (1996) Clin Pharmacokinet 31:9–28
3. Hideko H, Akiko O, Megumu H, Hiromitsu Y, Fumiko M, Kazuhiko N (2003) J Pharm Biomed Anal 30:1817–1824
4. Walan A (1989) Gastroenterol Hepatol 4:27–33
5. Jia H, Li W, Zhao K (2006) J Chromatogr B 837:112–115
6. Shimizu M, Uno T, Niioka T, Furukori NY, Takahata T, Sugawara K, Tateish T (2006) J Chromatogr B 832:241–248
7. Cass QB, Degani ALG, Cassiano NM, Pedrazolli J (2001) J Chromatogr B 766:153–160
8. Rezk NL, Brown KC, Kashuba ADM (2006) J Chromatogr B 844:314–321
9. Patel PH, Suhagia PN, Patel MM, Patel JR (2007) Chromatographia 65:743–748
10. Rambla-Alegre M, Esteve-Romero J, Carda-Broch S (2009) Anal Chim Acta 633:250–256
11. Sivakumar T, Manavalan R, Muralidharan C, Valliappan K (2007) Pharm Biomed Anal 43:1842–1848
12. Lou H, Yuan H, Ruan Z, Xu D, Zhou Q (2008) Chromatographia 67:795–799
13. Cheng FC, Ho HY, Hung LC, Chen CF, Tsai TH (2002) J Chromatogr A 949:35–42
14. Kanazawa H, Okada A, Matsushima Y, Yokota H, Okubo S, Mashige F, Nakahara K (2002) J Chromatogr A 949:1–9
15. Macek J, Klima J, Ptacek P (2007) J Chromatogr B 852:282–287
16. Wang J, Wang Y, Fawcett JP, Wang Y, Gu J (2005) J Pharm Biomed Anal 39:631–635
17. Perez-Ruiz T, Martinez-Lozano C, Sanz A, Bravo E, Galera R (2006) J Pharm Biomed Anal 42:100–106
18. Sluggett GW, Stong JD, Adams JH, Zhao Z (2001) J Pharm Biomed Anal 25:357–361
19. Gonzalez HM, Romero EM, Chavez TJ, Peregrina AA, Quezada V, Hoyo-Vadillo C (2002) J Chromatogr B 780:459–465
20. Salama F, El-Abasawy N, Abdel Razeq SA, Ismail MMF, Fouad MM (2003) J Pharm Biomed Anal 33:411–421
21. Wahabi AAM, Abdel-Razak O, Gazy AA, Mahgoub H, Moneeb MS (2002) J Pharm Biomed Anal 30:1133–1142
22. Sastry CSP, Naidu PY, Murty SSN (1997) Talanta 44:1211–1217
23. Ozaltin N, Kocer A (1997) J Pharm Biomed Anal 16:337–342
24. Karljikovic-Rajic K, Novovic D, Marinkovic V, Agbaba D (2003) J Pharm Biomed Anal 32:1019–1027
25. Espinosa Bosch M, Ruiz Sanchez AJ, Sanchez Rojas F, Bosch Ojeda C (2007) J Pharm Biomed Anal 44:831–844
26. El-Enany N, Belal F, Rezk M (2008) J Biochem Biophys Methods 70:889–896
27. Yardimci C, Ozaltin N (2001) Analyst 126:361–366
28. Ozaltin N, Temizer A (1994) Electroanalysis 6:799–803
29. McClean S, Okane E, Ramachandran ON, Smyth WF (1994) Anal Chim Acta 292:81–89
30. Belal F, El. Enany N, Rizk M (2004) J Food Drug Anal 12:102–109
31. Radi A (2003) J Pharm Biomed Anal 31:1007–1012
32. Yan JL (2006) J Appl Sci 6:1625–1626
33. Erk N (2003) Anal Biochem 323:48–53
34. Claussen JC, Franklin AD, Haque AU, Porterfield DM, Fisher TS (2009) Am Chem Soc Nano 3:37–44
35. Wang J (2005) Electroanalysis 17:7–14
36. Wang J (2006) Biosens Bioelectron 21:1887–1892
37. Wang J (2002) Trends Anal Chem 21:226–232
38. Salimi A, Sharifi E, Noorbakhash A, Soltanian S (2007) Biosens Bioelectron 22:3146–3153
39. You T, Niwa O, Chen Z, Hayashi K, Tomita M, Hirono S (2003) Anal Chem 75:5191–5196
40. Xing W, Li F, Yan Z, Lu GQ (2004) J Power Sources 134:324–330
41. Kamal H, Elmaghraby EK, Ali SA, Abdel-Hady K (2005) Thin Solid Films 483:330–339
42. Salimi A, Roushani M, Soltanian S, Hallaj R (2007) Anal Chem 79:7431–7437
43. Salimi A, Roushani M (2006) Electroanalysis 18:2129–2136
44. Salimi A, Roushani M, Hallaj R (2006) Electrochim Acta 51:1952–1960
45. Salimi A, Sharifi E, Noorbakhash A, Soltanian S (2007) Biophys Chem 125:540–549
46. Giovanelli D, Lawrence NC, Jiang L, Jones TGL, Compton RG (2003) Sens Actuators B 88:320–328
47. Radi A (2003) J Pharm Biomed Anal 33:687–692