Journal of Chemical and Pharmaceutical Research, 2016, 8(8):633-639



Research Article

ISSN: 0975-7384 CODEN(USA): JCPRC5

Synthesis and characterization of hierarchical nickel oxide (NiO) nanoparticles and its application in modified carbon paste electrode for electrochemical detection of biomolecules

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ABSTRACT

Nickel oxide (NIO) nanoparticles synthesized via hydrothermal method are reported and it is used for modification of carbon paste electrode (MCPE). The structural characterization of nanopowder by XRD clearly shows the formation of face-centered cubic (FCC) crystalline structure with high crystallinity. The morphological structure is characterized by field emission scanning electron microscope shows the formation of flake like structures. The modified electrode is used for the determination of dopamine, Folic acid (FA) and paracetamol separately using cyclic voltammetry. The voltammograms obtained during the oxidation studies revealed that nano NiO exhibits better catalytic function towards the oxidation of Dopamine (DA) and paracetamol (PC). The overlapping voltammetric response of both the biomolecules at the bare electrode gets resolved into well-defined voltammetric peaks with enhanced oxidation currents in 1×10^{-5} M DA in 0.2 M PBS pH 7.4.

Keywords: Nickel oxide nanoparticles; Modified Carbon Paste Electrode; Cyclic voltammetry; Biomolecules.

INTRODUCTION

Dopamine (DA) is one of the naturally occurring catechol amines in the mammalian central nervous system and it plays a key role in the function of central nervous, hormonal and cardiovascular systems [1-3]. Paracetamol (PC) or acetaminophen (N-acetyl-p-aminophenol or 4-acetamidophenol) is a non-steroidal anti-inflammatory drug and PC that finds widespread application for its strong antipyretic action and analgesics in pharmaceutical formulations [4]. Folic acid (FA) is B vitamin that helps build healthy cells as well as deficiency of FA is a common cause of anemia and is thought to increase the likelihood of heart attack and stroke. The ability to determine DA, PC and FC has been a major goal of electro-analytical application research.

Several methods have been proposed for the determination of biomolecules such as spectrophotometry, high performance liquid chromatography, chemiluminescence, capillary electrophoresis and electrochemical methods [5-9]. However, it is still a great challenge to develop simple, ecofriendly method for the determination of this biomolecules. In recent years electrochemical sensors has been widely applied due to the advantages such as high sensitivity, rapidity of response, simplicity, low cost, miniaturized and automated devices. The research activities in the preparation of electrochemical sensors for detecting biomolecules have dramatically increases over the past decades with the development of new materials and novel fabrication process[10-12]. Development of both selectivity and sensitivity are of equal importance in voltammetric procedure and also this would help in the treatment of several neurodegenerative diseases.

Nano scale based materials such as carbon nanotubes, Graphene, nanoparticles, nanocomposite are being used for several electro analytical applications. Electrochemical analysis using modified electrode is taking advantages from all the possibilities offered by nanocompounds easy to be detected by conventional electrochemical methods. This kind of modified electrode has gained increasing attention recently due to their potential applications to develop high performance electrochemical sensors [13-15].

Among various metal oxide nanoparticles, the hierarchical nickel oxides that are composed of nanometer-sized building blocks with the total size in the micrometer scale have many advantages in sensor. Their hierarchicallynonporous material provide high catalytic efficiency and active sites for Study Voltammetric Response of Biomolecules and the overall organized mesoporous metal oxide nanoparticles structure provides desirable mechanical strength[16].

Considering all the facts mentioned above, the present investigation reports a synthesis of hierarchical NiO by hydrothermal method characterized by XRD, SEM, TEM studies. The NiO modified electrode shows an increase in sensitivity towards DA. The MCPE was used for an electrochemical investigation of the low concentration of biomolecules in a phosphate buffer at pH 7.2 and also cyclic voltammetry experiments shows that NiO-modified carbon paste is stable enough in aqueous solution and it can be used as an electrochemical sensor for determination of biomolecules. This present approach has significant advantages such as low-cost, simple equipment, easy preparation, short reaction time and better repeatability. It is observed that the prepared NiO exhibit excellent sensitivity towards the determination of biomolecules.

EXPERIMENTAL SECTION

Materials

All chemicals were obtained from Sigma Aldrich or Merck with highest grade available and used without further purification. All solutions were prepared using double distilled water. All experiments were carried out at room temperature. The reactant,nickelnitrateNi(NO₃)₂·6H₂O ,Dopamine hydrochloride (DA), disodium hydrogen phosphate (Na₂HPO₄), sodium dihydrogen orthophosphate (NaH₂PO₄), Triton X-100 (C₁₄H₂₂O (C₂H₄O)_n), silicone oil, graphite powder (mm particle size). The stock solution of dopamine was prepared in 0.1 M perchloric acid, phosphate buffer of pH 7.4 prepared in double distilled water. Paracetamol and Folic acid obtained from Hi-media, Phosphate buffer solution (PBS) solutions all stock solutions were prepared with double distilled water.

Preparation of NiO nanoparticles

In a typical route, NiOnanoparticles weresynthesized *via* the hydrothermal method in the presence of Triton X-100. Experimental details are described as follows: 20 mlbasic precipitant 0.4M NaOH solution was slowly added into a 20 ml of 0.1 mol l^{-1} Ni(NO₃)₂·6H₂O solution containing 0.004 mol l^{-1} of Triton X-100 with constant stirring. After vigorous stirring for 3 h, the mixture was autoclaved at 200°C for 5h and cooling the reaction to room temperature; the precipitate was filtered from the solution and absolute alcohol several times and then dried in an oven at 50°C for 12h.

Instruments

XRD patterns were obtained on a Bruker D_2 Phaser XRD system and SEM was studied using scanning electron microscope (JEOL JSM 840). The cyclic voltammetric (CV) measurements were performed on a Model CHI 660D electrochemical work station (CH Instruments, Austin, USA). Electrochemical experiments were carried out in a three electrode cell system, which contained a bare carbon paste electrode (BCPE), CPE/ NiO, as the working electrode, an aqueous saturated calomel electrode (SCE) as the reference electrode and Platinum wire as the auxiliary electrode to measure current.

Preparation of bare carbon paste electrode (BCPE) and modified carbon paste electrode (MCPE)

The bare carbon paste electrode was prepared by hand mixing of graphite powder with silicon oil at a ratio of 70:30 (w/w) in an agate mortar to produce a homogenous carbon paste. The prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and then smoothed on a weighing paper. The electrical contact was provided by a copper wire connected to the end of the tube. MCPE was prepared by adding 2, 4, 6 and 8 mg NiO nanoparticles to above mentioned graphite powder and silicone oil mixture.

RESULTS AND DISCUSSION

Characterization of NiO

The purity and crystallinity of the as-synthesized NiO nanoparticles were examined by using powder X-ray diffraction (XRD) as shown in Fig.1. The peaks positions appearing at 2 theta is 37.2, 43.2, 62.8 and 75.39can be

readily indexed as (111), (200), (220), (311), and (104) crystal planes of the bulk NiO, respectively. All these diffraction peaks can be perfectly indexed to the face-centered cubic (FCC) crystalline structure of NiO not only in peak position, but also in their relative intensity of the characteristic peaks. It can be seen from Fig.1.That the diffraction peaks are low and broad due to thesmall size effect and incomplete inner structure of the particle and the average crystallite size, calculated by Scherrer formula was found to be less than 8 nm.



Fig. 1.Typical XRD image of NiO nanoparticles

The morphology of the prepared sample was observed by the scanning electron microscopy (SEM). Fig.2 shows a general SEMimage of the sample, which confirms its hierarchical structure consisting of a large number of quasi uniform flaked rice–like architectures. High magnification SEM images reveal that the flake-like architectures are built from many flexible and densely interlaced beads-like structures. Since the architectures are self-assembled from these nanobeads, the porous structure could be induced by inter aggregation of the building blocks.



Fig. 2.Typical SEM images of NiO at different magnifications

TEM was used to further investigate the microstructure of the as-synthesized NiO. It revealed the formation of nanoflakes with cubic crystal structure as shown in Fig.3 (a). It shows the presence of a large number of NiO particles with hexagonal shape and uniform size around 10–20 nm and well dispersed in the bulk material. Fig.3 (b) shows the electron diffraction pattern of the selected area of nanoparticles. The appearance of strong diffraction rings confirmed the formation of single crystalline cubic nickel oxide.



Fig. 3. (a) Typical TEM micrograph of NiO. (b) SAED patterns of NiO

Effect of NiOnanoparticles on MCPE for investigation of DA, PC and FA

In order to optimize the amount of NiO /CPE different concentration of the NiO nanoparticle in a CPE were used to determine the study electrochemical behavior of DA, PC and FA was also investigated in order to optimize the conditions. The 4 mg NiO/CPE response to the maximum current as compared with the 2, 6 and 8 mg of NiO nanoparticles as shown in Fig.4 and this optimized concentration is maintained further investigation.



Fig. 4.Cyclic voltmmogram of 5×10⁻⁵M DA at different concentration of NiOnanoparticles in MCPE

Electrochemical response of DA, PC and FA at BCPE and NiO/MCPE: Fig. 5a, 5b and 5c shows the cyclic voltammograms obtained for the electrochemical studies of 1×10^{-5} M DA, 1.0×10^{-6} M PC and 5×10^{-5} M FAits voltammogramm was recorded in the potential range of -0.2 to 0.6 vs. SCE in the 0.2 M phosphate buffer solution of pH 7.4 at the BCPE and the MCPE prepared with NiO nanoparticles were measured at a scan rate of 50 mV s⁻¹ by CV technique. The corresponding peak potential differences [Δ Ep=0.0723 V] and [Δ Ep=0.1145 V] for the BCPE (black line) and the NiO nanoparticles MCPE (red line) are Showed well-defined redox peaks at both the electrodes forDA. At the BCPE the anodic peak potential (Epa) 0.1667 V and the cathodic peak potential (Epc) 0.0944 v as well as the relative DA peak currents significantly increased at the MCPE with the anodic peak potential 0.1904 V and the corresponding cathodic peak potential is 0.0759 V respectively. The oxidation peak potential is 0.1843 V respectively. At the bare CPE the cyclic voltammogram of FA shows an oxidation peak potential at 701 mV. At NiO /MCPE of FA was obtained with the oxidation peak potential occurs at 680mV. The result indicates NiO /MCPE exhibit good electro catalytic activity than BCPE and NiO /MCPE exhibit enhanced current response than the BCPE.



Fig. 5. Cyclic voltmmogram of (a) DA (b) 1.0×10^{-6} M PC (c) $\times 10^{-5}$ M FA in 0.2 M phosphate buffer solution, pH 7.2 at bare CPE and MCPE of 5×10^{-5} M DA with scan rate 50 mV s⁻¹



Fig. 6.Cyclic voltmmogram of 1.0 ×10⁻⁶ M PC in 0.2 M phosphate buffer solution using NiO/MCPE at different scan rates

Effect of scanrate on the peak current PC at NiO/MCPE

The effect of scan rate for PC in phosphate buffer solution at pH 7.4 was studied by CV at NiO /MCPE. The Fig. 6 show an increase in the redox peak current at a scan rate of 0.05–0.500 V s⁻¹ for NiO /MCPE indicating that direct electron transfer between PC and the modified electrode surface. The graph obtained exhibited good linearity

between the scan rate (v) and the redox peak current (Fig. 7) for the MCPE with correlation coefficients of (R^2) was 0.99, which indicates that the electron transfer reaction was diffusioncontrolled process. The MCPE prepared with the flake-shaped NiO nanoparticles exhibits a higher electrode surface area, a higher electron-transfer rate constant and compared with the BCPE. Therefore, the MCPE prepared with NiO nanoparticles have small size particles and high surface area of electrode may be leads to electrocatalytic effect on PC [17]. Therefore MCPE prepared from flake-shaped NiO nanoparticles used as an electrochemical detection of PC at physiological pH 7.2.



Fig. 7.Typical graph showing the linear relationship between the anodic peak current and scan rate

Simultaneous determination PC in the presence of FA

The determination of PC using a BCPE suffers from interference with FA due to their closely related oxidation potentials [18]. The feasibility of the PC selective determination in the presence of FA at the NiO/MCPE was easier, because the large pore volume of NiO /MCPE provides a large specific area leading to the enhancement in peak current. The determination of PC in the presence of 5 mM FA was performed at the NiO/MCPE (Fig. 8). At the BCPE the anodic peak potential (Epa) 0.4116 V and PC peak currents significantly increased at the NiO/MCPE with the anodic peak potential 0.4283 V. These results prove that the MCPEsensor was effective in simultaneous sensing of PC and FA.



Fig. 8.Cyclic voltammograms obtained for the determination of PC, in the presence of 5×10^{-5} M FA in 0.2 M phosphate buffer solution at pH 7.2 using bare CPE and NiO /MCPE at scan rate 50 mV s⁻¹

CONCLUSION

The synthesized NiO/MCPE improved the sensitivity of electrode and acting as a good electrochemical sensor for the detection of DA, FA and PC. Cyclic voltammetry measurements revealed a reasonably fast electron transfer and

advantage of this method is convenient for synthesis of NiO nanoparticles in normal laboratory conditions, in low cost. With its high selectivity, regeneration of the electrode surface and very easy preparation of the NiO/MCPE and the good reproducibility of the voltammetric response make the prepared modified metal oxides system very useful in the construction of simple devices in the medicine field for the diagnosis of dopamine deficiency. It is expected that this current synthetic method extended to many metal oxides for synthesis and their modified electrode used as sensor application for determination of biological active compounds.

Acknowledgments

The authors wish to thank Dr. B.E. Kumaraswamy, Department of Industrial Chemistry, Kuvempu University, for his invaluable suggestions and moral support. The authors are also thankful toK.S. Institute of Technology, Bangalore for providing lab facility.

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