

Full Paper

The Simultaneous Electrochemical Determination of Dopamine and Uric acid at Ni_{0.02}Sn_{0.98}O₂ Nanoparticles Modified Carbon Paste Electrode by Cyclic Voltammetric Technique

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Abstract- The electrochemical method using Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode (NSNMCPE) for the determination of dopamine (DA) and uric acid (UA). The Ni_{0.02}Sn_{0.98}O₂ nanoparticles were synthesized by gel combustion method. These synthesized Ni_{0.02}Sn_{0.98}O₂ nanoparticles were characterized by XRD and SEM. Then the carbon paste electrode is modified with the synthesized Ni_{0.02}Sn_{0.98}O₂ nanoparticles by grinding method. The surface morphology of NSNMCPE was confirmed by SEM. The NSNMCPE was successfully used to study the electrochemical investigation of DA and UA in 0.1 M phosphate buffer solution (PBS) of pH 7.0 and pH 6.0 by cyclic voltammetric technique (CV). The low detection limit (LOD) of DA and UA were found to be 0.831×10^{-5} M and 1.11×10^{-5} M and the low quantification limit (LOQ) of DA and UA were 2.77×10^{-6} M and 0.371×10^{-6} M respectively. The NSNMCPE was used for the simultaneous determination of DA and UA, the separation of the overlapping voltammograms of dopamine and uric acid at modified electrode in a mixture is successfully carried by using cyclic voltammetric technique. The proposed method was successfully applied for the determination of DA and UA due to its good sensitivity, lower detection limit and ease of preparation of the

NSNMCPE allows the development of a highly sensitive voltammetric sensor for the determination of DA and UA.

Keywords- Dopamine (DA) Uric acid (UA), Ni_{0.02}Sn_{0.98}O₂ nanoparticles, Carbon paste electrode, Cyclic Voltammetry

1. INTRODUCTION

Dopamine (DA), also known as "4-(2-aminoethyl) benzene-1, 2-diol", belongs to a member of the catecholamine family. Since the discovery of dopamine as a neurotransmitter in the late 1950s, dopamine has become the most widely studied catecholamine [1]. Uric acid (UA) (2, 6, 8-trihydroxypurine) is the primary product of purine metabolism in the human body. It is a diprotic acid with pK_{a1}=5.4 and pK_{a2}=10.3 [2]. Thus in strong alkali at high pH it forms the dually charged full urate ion, but at biological pH it forms the singly charged hydrogen or acid urate ion as its pK_{a2} is greater than the pK_{a1} of carbonic acid. As its second ionization is so weak the full urate salts tend to hydrolyse back to hydrogen urate salts and free base at pH values around neutral. It is aromatic because of the purine functional group.

As a bicyclic, heterocyclic purine derivative, uric acid does not protonate in the same manner as do carboxylic acids, whereas most organic acids are deprotonated by the ionization of polar hydrogen-to-oxygen bond, usually accompanied by some form of resonance stabilization, this acid is deprotonated at a nitrogen atom and uses a tautomeric keto/hydroxy group as an electron-withdrawing group to increase the pK_{a1} value. The five membered ring also possesses a keto group (in the 8 position), flanked by two secondary amino groups (in the 7 and 9 positions), and deprotonation of one of these at high pH could explain the pK_{a2} and behavior as a diprotic acid [3].

Preparation of these materials in the nanoscale size range is more interesting due to the increased surface-to-volume ratio that might affect the structural and most other physical properties. Transition-metal (TM) doping has been proposed to introduce magnetic functionality in conventional semiconductors [4,5]. Nanoparticles of tin oxide have been synthesized through different chemical routes, such as precipitation [6,7], sol-gel [8,9], hydrolytic [10], and polymeric precursor [11] methods among others. In this work, we synthesize Ni-doped SnO₂ nanoparticles by gel combustion method because this method has some advantages such as precise control over the stoichiometry, high temperature synthesis, high purity and high chemical homogeneity.

Extreme abnormalities of DA and UA concentrations levels may lead to several diseases and it is essential to develop a simple and rapid method for the determination of both DA and UA for routine analysis. The grinding, adsorption or coating of polymeric species or films onto the surface of conventional substrates has become a preferred approach for the construction of chemically modified electrodes (CMEs). The grinding modified electrodes have attracted great attention, because of their good stability, reproducibility and their wide

applications in the fields of chemical sensors and biosensor. A variety of examples of the electrochemical determination of DA and UA along with AA have been proposed. These include a carbon paste electrode using zinc oxide nanoparticles and a new ferrocene-derivative modified carbon paste electrode [12], voltammetric sensor employing CuFe_2O_4 nanoparticles and room temperature ionic liquids [13], A novel modified carbon paste electrode based on NiO/CNTs nanocomposite and (9, 10-dihydro-9, 10-ethanoanthracene-11, 12-dicarboximido)-4-ethylbenzene-1, 2-diol as a mediator [14], FePt/CNTs nanocomposite/*N*-(4-hydroxyphenyl)-3,5-dinitrobenzamide modified carbon paste electrode [15], Modified multiwall carbon nanotubes modified electrode [16], Ethynylferrocene–NiO/MWCNT nanocomposite modified carbon paste electrode [17], ZnO/CNT nanocomposite room temperature ionic liquid modified carbon paste electrode [18], Poly (L-Tyrosine)/ SnO_2 Nanoparticles Modified Carbon Paste Electrode [19].

In continuation of our work on the modification of carbon paste electrodes we intended for the $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modifier and applied for the electrochemical investigation for dopamine and uric acid simultaneously.

2. EXPERIMENTAL SECTION

2.1. Reagent and Chemicals

Tin (II) chloride dehydrate ($\text{SnCl}_2 \cdot \text{H}_2\text{O}$, 99.99%, Merck), Nitric acid (HNO_3 , 70%, Merck), Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99.5%, Merck), Nickel chloride Hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), Potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6]$ and UA solutions were prepared by dissolving in double distilled water. DA was prepared by dissolving in 0.1 M perchloric acid (HClO_4) solution, 0.1 M potassium chloride (KCl) was used as supporting electrolyte for all analytes. Chemicals mentioned above were all purchased from Fluka and were analytical grade.

2.2. Apparatus and Procedure

The electrochemical experiments were carried out using an Electroanalyser model EA-201 chemlink system. All experiments were carried out in a conventional three-electrode system. The electrode system contained a working carbon paste electrode, homemade cavity of 3 mm diameter, a platinum wire as counter electrode and saturated calomel electrode as reference electrode. $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode was prepared by grinding the 10 mg of $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles with 70% graphite powder (50 μm particle size was purchased from sdfine-chem Ltd) and 30% silicon oil (Himedia) in an agate mortar by hand mixing for about 30 minute to get homogenous $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles MCPE. The paste was packed into the cavity of CPE and smoothed on weighing paper. The bare CPE was prepared without adding modifier.

2.3. Synthesis of Ni_{0.02}Sn_{0.98}O₂ nanoparticles

Ni_{0.02}Sn_{0.98}O₂ nanoparticles was synthesized by gel combustion method. The materials used are tin (II) chloride dehydrate, 6.2 mole of nitric acid which is used as an oxidizer and mixed in an appropriate ratio to form a tin nitrate solution, then 1.5 mole of citric acid which acts as fuel and 0.02 ml Nickel chloride Hexahydrate (NiCl₂.6H₂O) was added to solution and the solution was heated at 90 °C in a Pyrex vessel with constant stirring. When the temperature was raised to about 300 °C, the polymeric precursor underwent a strong, self-sustaining combustion reaction occurs with evolution of large volume of gases and swelled into voluminous and foamy ashes. The entire combustion process occurs in a few seconds. The produced ashes were then calcined at 800°C (for 1 h).The process was carried out, until the complete decomposition of the carbonaceous residues. Then the white powder Ni_{0.02}Sn_{0.98}O₂ nanoparticles were obtained [20].

3. RESULTS AND DISCUSSION

3.1. Characterization of synthesized Ni_{0.02}Sn_{0.98}O₂ nanoparticles by XRD and SEM

Crystalline structure and crystallite size of Ni_{0.02}Sn_{0.98}O₂ nanoparticles were analyzed by Cu-K_α X-ray radiation ($\lambda=1.5418\text{Å}$) in 2θ range from 20° to 80°, operating at 30 kV and 15 mA. The scan rate was 5°/min.). XRD patterns of Ni_{0.02}Sn_{0.98}O₂ nanoparticles annealed at 800 °C for 1hr as shown in Fig. 1, the average grain size was calculated using the Scherer relation,

$$d = 0.89 \frac{\lambda}{\beta \cos \theta} \quad (1)$$

Where d is the crystallite size, λ is the wavelength of X-rays, β is the full width of half maximum and 2θ is the diffraction peak angle [21], the (110) peak is used to calculate the crystallite sizes.

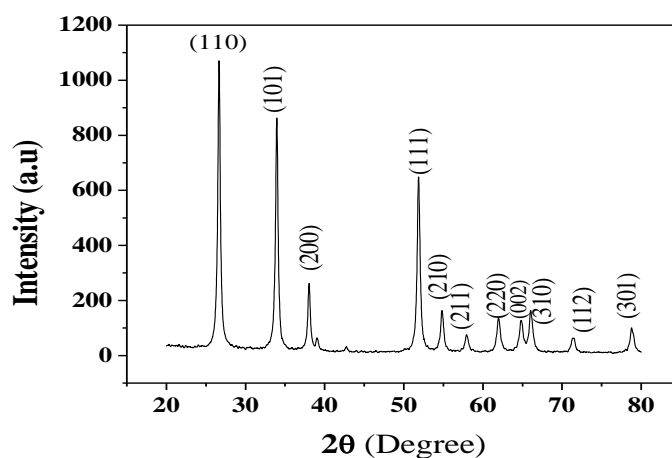


Fig. 1. XRD images of synthesized of Ni_{0.02}Sn_{0.98}O₂ nanoparticles

The crystallite sizes of $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles are found to be 23.03 nm by using Scherer formula. The surface morphology and shape of the nanoparticles of powdered samples were investigated by scanning electron microscope (SEM) (Hitachi Model S-3200N). Fig. 2 shows the typical SEM image of the $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles.

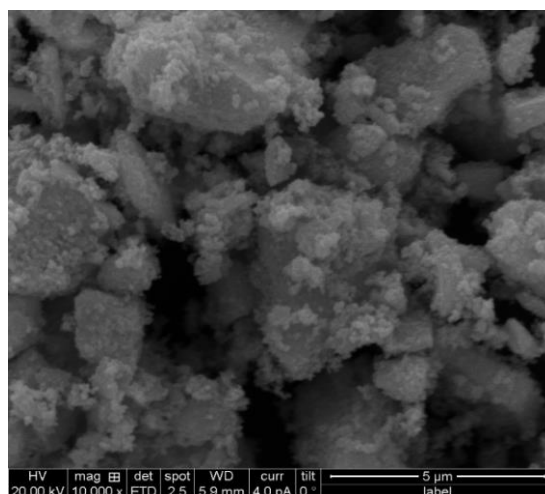


Fig. 2. SEM image of synthesized $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles

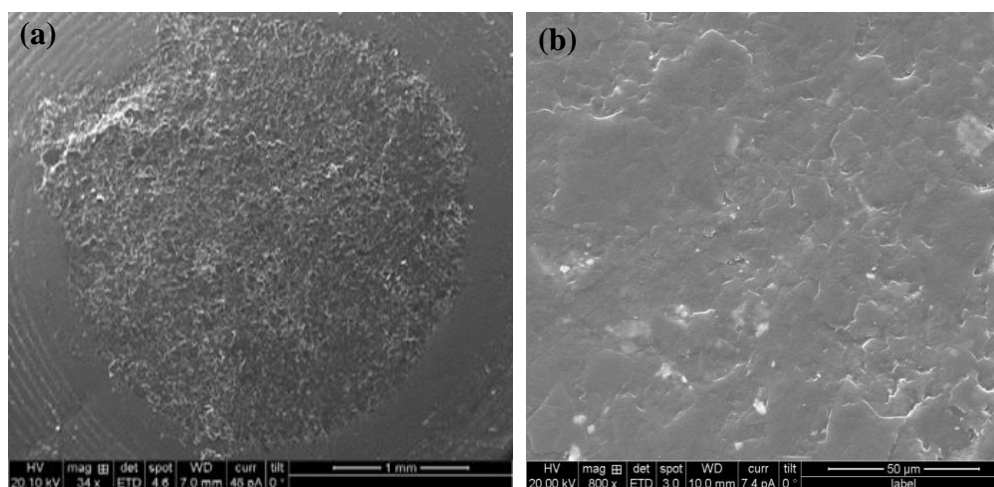


Fig. 3. (a) SEM image of bare carbon paste electrode; (b) SEM image of $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode

3.2. SEM Characterization of $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode

The morphology of the CPE and NSNMCPPE was characterized by scanning electron microscope (SEM) and shown in Fig. 3a and 3b respectively. Smooth surface was observed on bare CPE surface. In the modified electrode the formation of spindle-like nanostructures

not only enlarges the surface area of the electrode, but also improves the electron transfer rate between the electrode surface and the bulk solution, which has been confirmed by the performance of NSNMCPE in electrochemical investigation of $K_4[Fe(CN)_6]$ system.

3.3. Electrochemical response of potassium ferrocyanide at $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode

Fig. 4 shows the electrochemical behavior of 0.1 mM potassium ferrocyanide ($K_4[Fe(CN)_6]$) in 0.1 M KCl at bare carbon paste electrode (BCPE) curve 'b' and at $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode (NSNMCPE) curve 'a' respectively. The curve 'b' shows the cathodic peak current I_{pc} 2.8 μA of E_{pc} 24.2 mV and anodic peak current I_{pa} 4.3 μA of E_{pa} 353 mV at BCPE. Whereas, for the NSNMCPE the cathodic peak current I_{pc} 15.0 μA of E_{pc} 54 mV and anodic peak current I_{pa} 16.3 μA of E_{pa} 291 mV has been observed. The enhancement of peak current showed excellent catalytic ability of NSNMCPE. The surface area of bare carbon paste electrode is 0.0312 cm^2 , whereas the effective surface area of the modified electrode was found to be 0.0403 cm^2 .

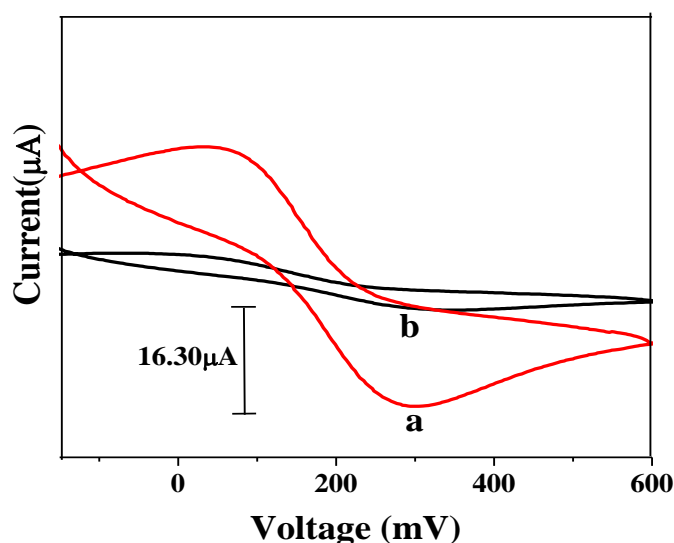


Fig. 4. Comparison of 0.1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution at $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode (a) and bare carbon paste electrode (b)

3.4. Electrochemical behavior of dopamine (DA) at $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode

The electrochemical behavior of dopamine (DA) was investigated in 0.2 M phosphate buffer solution (PBS) of pH 7 at NSNMCPE using cyclic voltammetric technique. Fig. 5 shows cyclic voltammograms of 1 mM DA at bare CPE (curve 'b') and at NSNMCPE (curve 'a'). The curve 'c' represents the cyclic voltammogram of blank solution at NSNMCPE. The

Fig. 5 confirmation the modification of bare carbon paste electrode. Above studies showed that redox peaks. The oxidation peak at 266 mV potential with peak current of 3.9 μA and reduction peak at 80 mV potential with current peak of 1.8 μA at bare CPE, whereas an oxidation peak at 257 mV potential with a peak current of 18.44 μA and reduction peak at 101 mV potential with current peak of 6.4 μA at NSNMCPE respectively in the potential range from -200 to 600 mV. The peak was observed in the reverse scan, suggesting that the electrochemical reaction is a totally quasireversible process and the redox peak at the bare CPE is broad due to slow electron transfer, while the response was considerably improved at NSNMCPE and the peaks potentials shifted to negative direction, the shape of the peaks turns sharper and the peak current increased significantly.

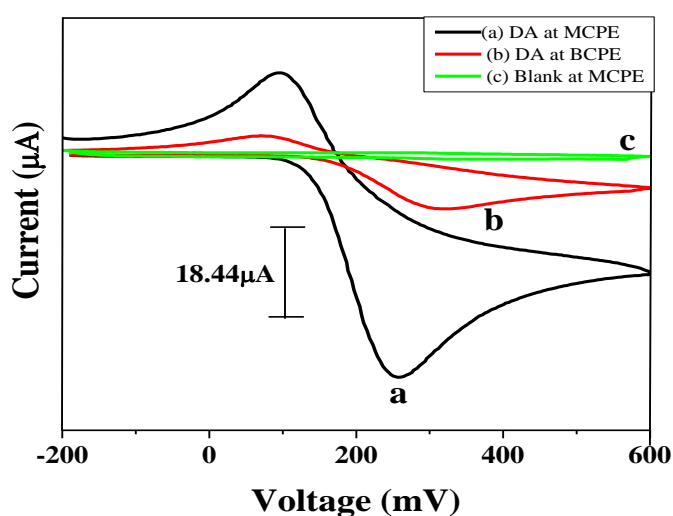


Fig. 5. Comparison of 1 mM DA at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode (a), bare carbon paste electrode (b) and blank solution in phosphate buffer solution at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode (c); pH 7, scan rate 50 mVs^{-1}

3.5. Electrochemical behavior of uric acid (UA) at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode

The electrochemical behavior of UA was investigated in 0.2 M phosphate buffer solution of pH 6 at NSNMCPE using cyclic voltammetric technique. Fig. 6 shows cyclic voltammograms of 0.1 mM UA at bare CPE (curve 'a') and NSNMCPE (curve 'b'). The curve 'c' represents the cyclic voltammogram of blank solution at NSNMCPE. Above studies showed that only one oxidation peak at 433 mV potential with peak current of 1.18 μA at bare CPE, whereas an oxidation peak at 432 mV potential with peak current of 1.99 μA at NSNMCPE, in the potential range from 100 to 600 mV. No reduction peak was observed in the reverse scan, suggesting that the electrochemical reaction is a totally irreversible process and the oxidation peak at the NSNMCPE is broad due to slow electron transfer, while the

response was considerably improved at modified electrode and the peak potentials shifted to negative direction, the shape of the peak turns sharper and the peak current increased significantly.

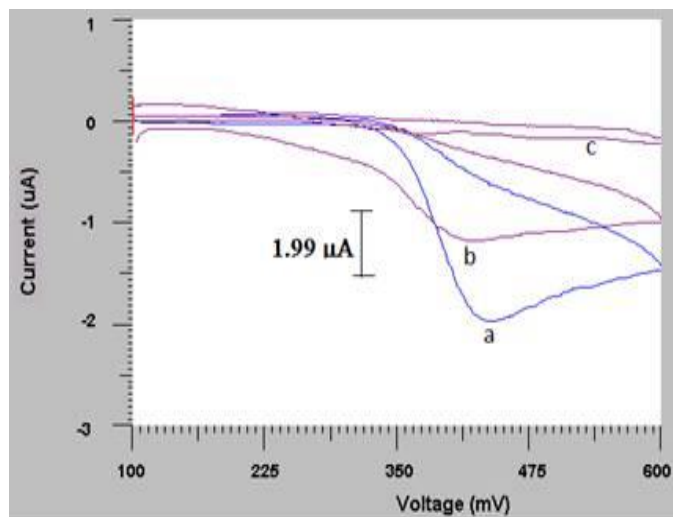


Fig. 6. Comparison of 0.1 mM UA at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode(a), bare carbon paste electrode (b) and blank solution in phosphate buffer solution at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode(c); pH 6, scan rate 10 mVs^{-1}

3.6. Effect of pH on DA and UA

The electro oxidation of DA was studied at 0.1 mM stock solution in 0.2 M phosphate buffer solution over pH range from 2.5 to 8.5 at a scan rate of 50 mVs^{-1} at NSNMCPE using cyclic voltammetric technique. The oxidation peak current increases with increase of pH from 2.5 to 7 and becomes maximum and peak potential shifted negatively. While pH beyond 7, a great decrease of the oxidation peak current has been observed, then it decreased gradually with the further increase in pH of the solution is shown in Fig. 7a and the oxidation peak potential decrease within increase of pH is shown in Fig. 7b. The corresponding linear regression equation is

$$E_{\text{pa}}(\text{mV}) = 742.609 - 72.208 \text{ pH} \quad (R = 0.99687) \quad (2)$$

The value of this slope is in close agreement with the theoretical value of 59 mV/pH at 25° for a $2e^-$ transfer process. Other researchers also have reported $2e^-$ transfer oxidation process in DA [22,23].

The effect of pH on electrooxidation of UA has been studied by using 0.1 mM stock solution of UA in 0.2 M PBS in pH range from 3 to 9 at a scan rate 50 mVs^{-1} at NSNMCPE using cyclic voltammetric technique. The anodic peak current decreases with increase of pH from 3 to 5.5 and becomes maximum and peak potential shifted negatively at pH 6.

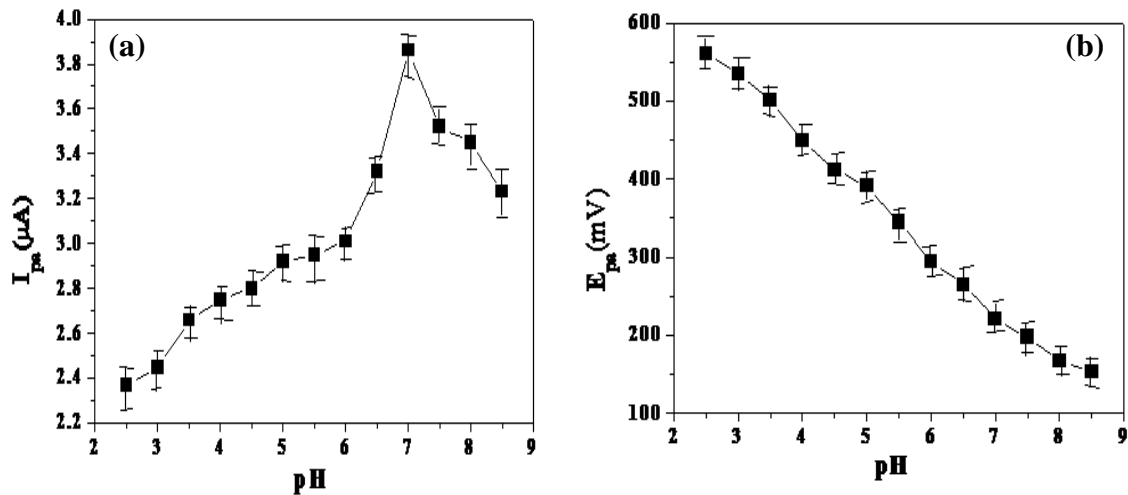


Fig. 7. (a) Plot of anodic peak current vs. pH (2.5-8.5) of 0.1 mM DA at Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode; (b) Plot of anodic peak potential vs. pH (2.5-8.5) of 0.1 mM DA at Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode

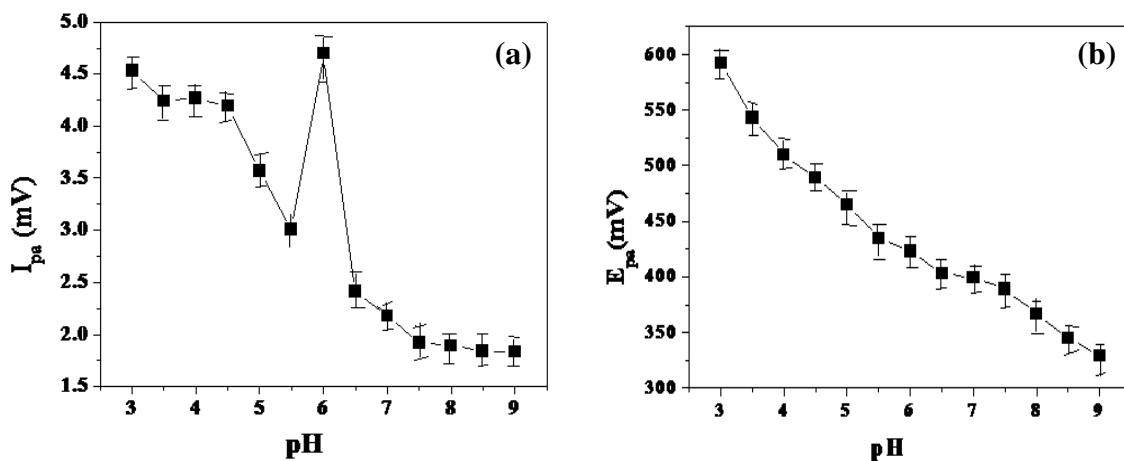


Fig. 8. (a) Plot of anodic peak current vs. pH (3-9) of 0.1 mM UA at Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode; (b) Plot of anodic peak potential vs. pH (3-9) of 0.1 mM UA at Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode

While pH beyond 6, a great decrease of the oxidation peak current has been observed, then it decreased gradually with the further increase of pH is shown in Fig. 8a and the oxidation peak potential decrease within increase of pH shown in Fig. 8b respectively. The corresponding linear regression equation is

$$E_{pa}(\text{mV})=675.24-39.640 \text{ pH} \quad (R=0.98069) \quad (3)$$

The negative slope of 39.640 was close to the theoretical value indicated that the electrons and protons involved in the oxidation of UA were equal (1:1).

3.7. Effect of scan rate on DA and UA

Useful information involving electrochemical mechanism usually can be acquired from the relationship between peak current and scan rate. Therefore, the effect of scan rates on the electrochemical response of 0.1 mM dopamine at NSNMCPE was studied at different scan rates including 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300 mVs^{-1} by CV and the cyclic voltammograms were shown in Fig. 9a. The linear relationship with a correlation coefficient of 0.99771 obtained between the anodic peak current and square root of scan rate in the range of 25–300 mVs^{-1} is shown in Fig. 9b. The corresponding linear regression equation is

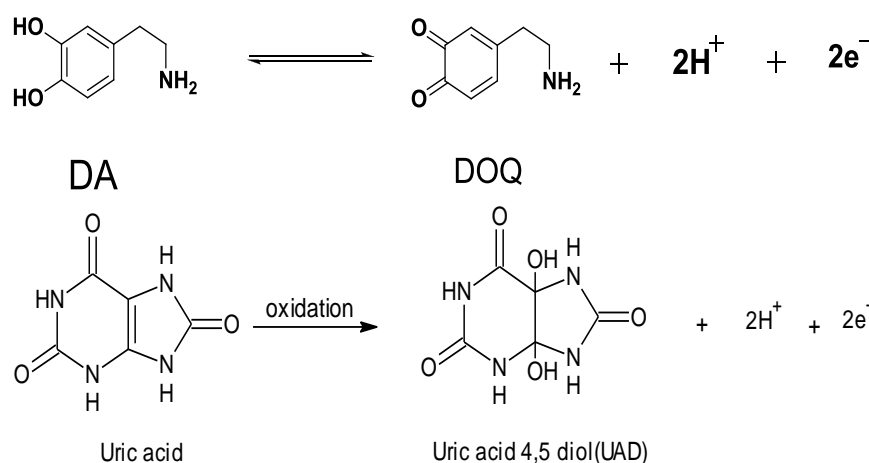
$$I_{\text{pa}}(\mu\text{A})=1.303v^{1/2}+10.856 \quad (R=0.9977) \quad (4)$$

This revealed that a diffusion controlled process occurring at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode.

Similarly the effect of scan rates on UA has been discussed. The electrochemical response of 0.1 mM UA at NSNMCPE was studied at different scan rates including 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mVs^{-1} by CV and the cyclic voltammograms were shown in Fig. 10a. The linear relationship with a correlation coefficient of 0.99387 was obtained between the anodic peak current and square root of scan rate in the range of 10–100 mVs^{-1} which is shown in Fig. 10b. The corresponding linear regression equation is given by

$$I_{\text{pa}}(\mu\text{A})=0.4180 v^{1/2}+0.444 \quad (R=0.9959) \quad (5)$$

which revealed that a diffusion controlled process occurring at NSNMCPE.



Scheme 1. Oxidation of DA and UA

According to Laviron's theory [24], the slope is equal to $RT/\alpha n_{\alpha}F$. Then the value of αn_{α} found to be 0.4542. As for a totally quasi-reversible electrode reaction process of dopamine

and irreversible electrode reaction process of uric acid. The n_a were calculated as 2.0238 and 1.908 respectively.

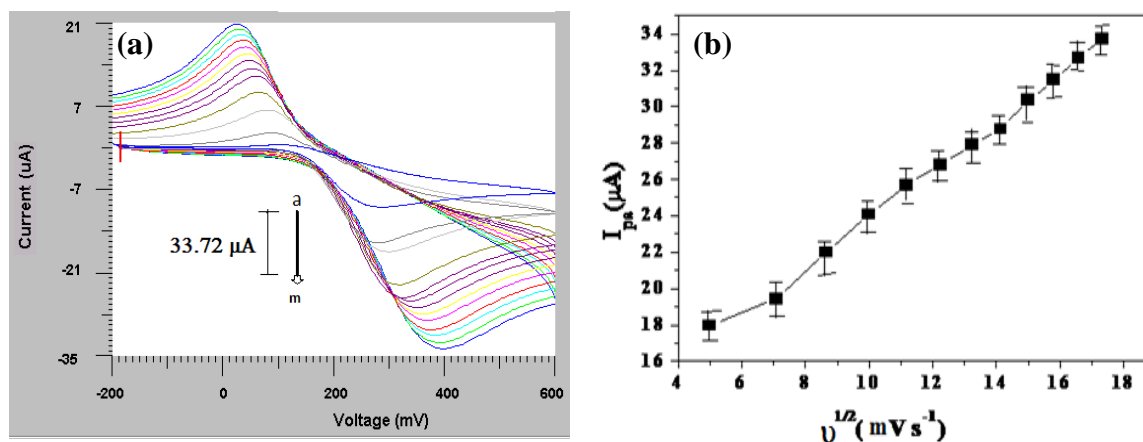


Fig. 9. (a) Cyclic voltammograms of 0.1 mM DA at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ modified carbon paste electrode with different scan rates (a) 25, (b) 50, (c) 75, (d) 100, (e) 125, (f) 150, (g) 175, (h) 200, (i) 225, (j) 250 and (k) 300 mVs^{-1} ; (b) Plot of anodic peak current vs. square scan rates of DA at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode

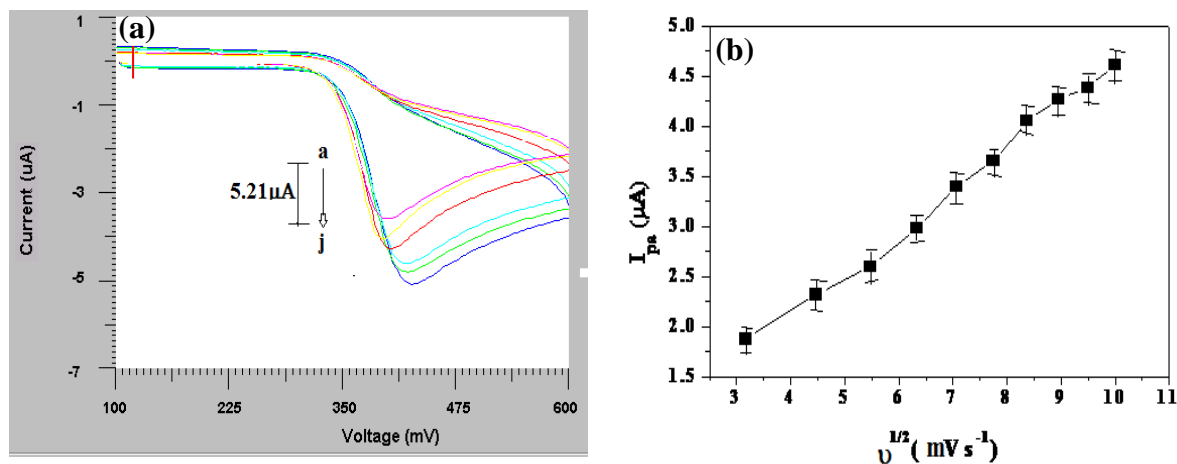


Fig. 10. (a) Cyclic voltammograms of 0.1 mM UA at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode with different scan rates (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80 (i) 90 and (j) 100 mVs^{-1} ; (b) Plot of anodic peak current vs. square root of scan rates of UA at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode

This indicated that two electrons were involved in the oxidation process of dopamine and uric acid at NSNMCPE. Since the equal number of electron and proton took part in the oxidation of dopamine and uric acid, therefore two electrons and two protons transfer were involved in the electrode reaction process. The electrochemical reaction process for dopamine and uric acid at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode can therefore be summarized as in scheme 1.

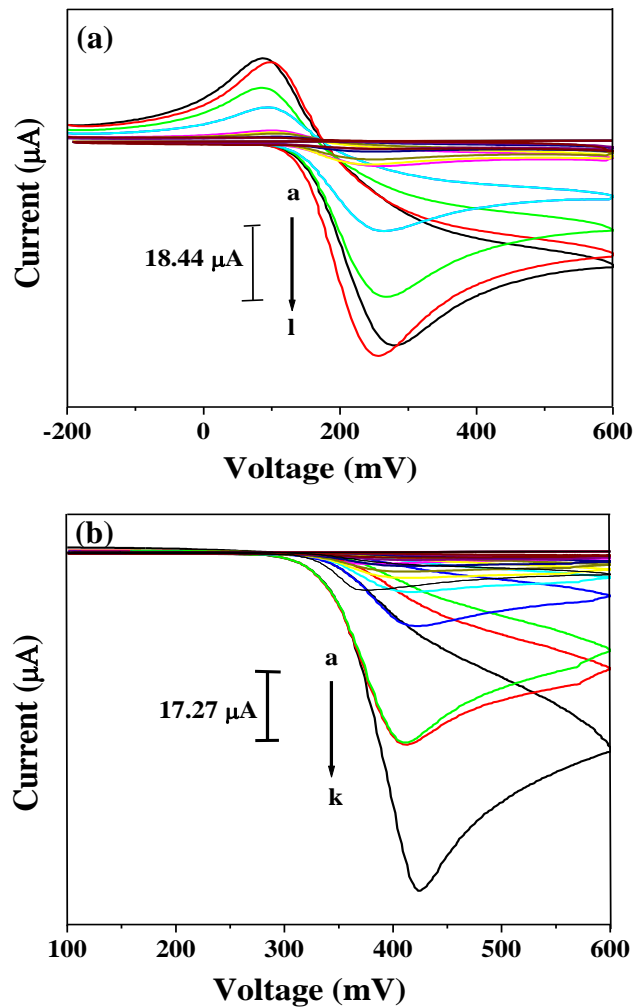


Fig. 11. (a) Effect of variation of concentration of DA (a) 1×10^{-5} M, (b) 2×10^{-5} M, (c) 4×10^{-5} M, (d) 6×10^{-5} M, (e) 8×10^{-5} M, (f) 1×10^{-4} M, (g) 2×10^{-4} M, (h) 4×10^{-4} M, (j) 6×10^{-4} M (k) 8×10^{-4} M, (l) 1×10^{-4} M, on anodic peak current at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode; scan rate 50 mVs^{-1} ; **(b)** Effect of variation of concentration of UA (a) 1×10^{-5} M, (b) 2×10^{-5} M, (c) 4×10^{-5} M, (d) 6×10^{-5} M, (e) 8×10^{-5} M, (f) 1×10^{-4} M on anodic peak current at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode; scan rate 50 mVs^{-1}

3.8. Calibration of Dopamine and Uric acid concentration

A series of dopamine and uric acid solutions of 1.0×10^{-5} to 1.0×10^{-3} M were prepared in phosphate buffer solution to investigate the relationship between the anodic peak current (I_{pa}) and concentration of dopamine and uric acid at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode at a scan rate of 50 mVs^{-1} by CV. The obtained cyclic voltammogram of dopamine and uric acid were shown in Fig. 11a and 11b respectively. A linear relationship has obtained on plotting I_{pa} vs concentration of DA and UA which is shown in Fig. 12a and

Fig. 12b respectively. This is explained on the basis of linear regression equations for DA and UA respectively.

$$I_{pa} (\mu A) = 18.938 C (10^{-5} M) + 0.0276 \quad (R=0.9971) \quad (6)$$

$$I_{pa} (\mu A) = 18.005 C (10^{-5} M) + 0.0027 \quad (R=0.9949) \quad (7)$$

The limit of detection (LOD) and limit of quantification (LOQ) were 0.831 μM , 2.770 μM for DA and 1.11 μM , 3.71 μM for UA respectively.

The LOD and LOQ were calculated on the peak current using the following equations are $LOD=3S/M$ and $LOQ=10S/M$

Where, S is standard deviation and M is the slope of calibration plot.

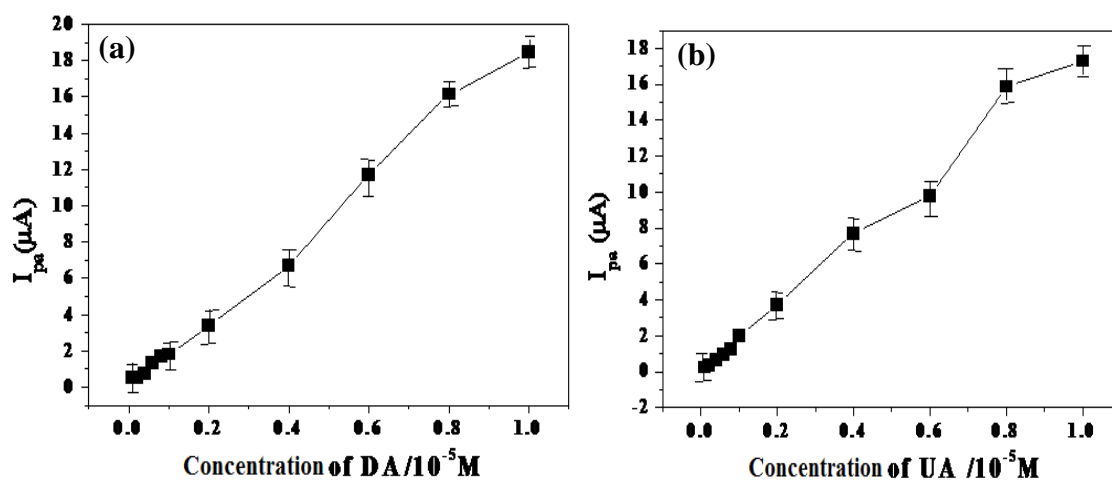


Fig. 12. (a) Plot of anodic peak current vs. concentration of DA at $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode; (b) Plot of anodic peak current vs. concentration of UA at $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode

3.9. Simultaneous determination of DA and UA at $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode

The objective of our work was the simultaneous determination of DA and UA. Fig. 13 shows the cyclic voltammograms of DA and UA co-existing in phosphate buffer solution of pH 7 at the bare carbon paste electrode and $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode respectively. The curve 'b' shows the cyclic voltammogram of the solution containing 0.2 mM DA and 0.5 mM UA mixture at the bare carbon paste electrode. It exhibits one broad peak for both the analytes and indicates that the bare carbon paste electrode fails to separate the voltammetric signals of DA and UA. The curve 'a' of Fig. 13 shows the cyclic voltammogram of the oxidation of 0.2 mM DA and 0.5 mM UA mixture at $Ni_{0.02}Sn_{0.98}O_2$ nanoparticles modified carbon paste electrode. It exhibits two well-defined oxidation peaks at 270 and 315 mV potential corresponding to the oxidation of DA and UA

respectively. The difference between the anodic peak potential of DA and UA was about 45 mV. Therefore, $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode can be effectively employed to separate DA in the presence of UA.

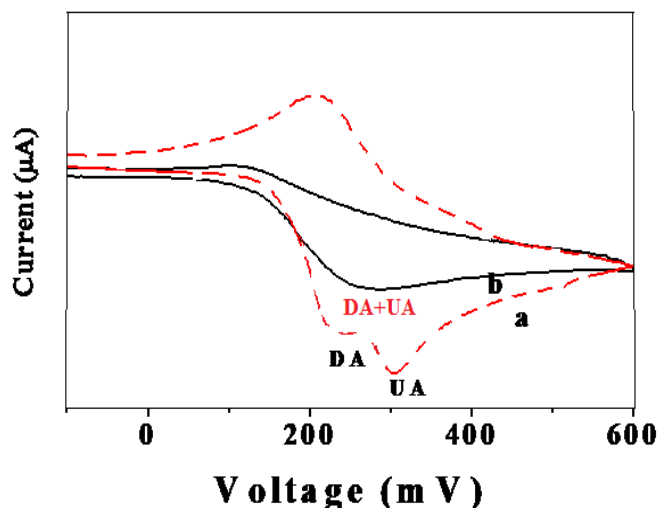


Fig. 13. Cyclic voltammogram at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode (a) and (b) bare CPE in presence of 0.5 mM DA and 0.2 mM UA in 0.2 M PBS (pH 7.0); scan rate 50 mVs^{-1}

3.10. Interference study

The possible influence of AA which coexists with DA and UA in body fluids on the electrochemical behavior of DA and UA has been investigated.

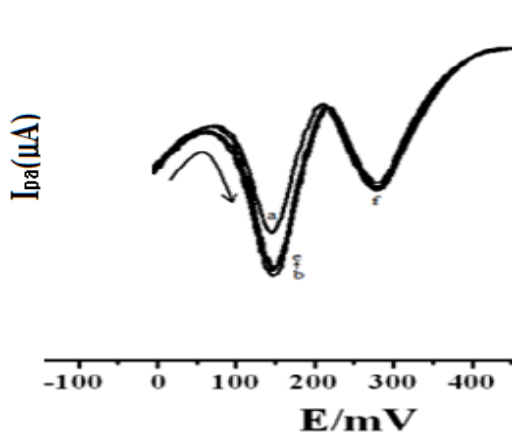


Fig. 14. Differential pulse voltammograms of DA and UA in presence of AA at $\text{Ni}_{0.02}\text{Sn}_{0.98}\text{O}_2$ nanoparticles modified carbon paste electrode in 0.2 M PBS (pH 7.0) with the scan rate 50 mVs^{-1} . (a) 0.1 mM DA, (b to e) 0.1 mM DA+0.1, 0.2, 0.3 and 0.4 mM AA, and (f) 0.1 mM UA

The effect of increasing concentration of AA on DA and UA at modified electrode was carefully examined by differential pulse voltammetry. Fig. 14 shows the differential pulse voltammograms of mixed solution of 0.1 mM DA, 0.1 mM UA and varying concentrations of AA (from b to e, 0.1, 0.2, 0.3 and 0.4 mM). As can be seen from the Figure, the oxidation peak current of DA changes and the peak potential did not change much. However, when the concentration of AA exceeds 0.4 mM this interference is constant and there is no change in the oxidation currents of DA. This means that in the extracellular fluid of central nervous system, where the AA level is usually present more than 100-folds of magnitude larger than DA, Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode can be used for the determination of DA and also in real samples. As shown in the figure the presence of AA has no effect on the UA signal. Moreover, AA shows no reduction peak in pH 7 of 0.2 M PBS at the modified electrode by DPV. This can also be used for the simultaneous determination of DA in presence of AA.

3.11. Analytical application

The practical application of the modified electrode was illustrated by simultaneous determination of DA and UA in injection and human urine sample respectively. 1 ml of DA hydrochloride injection USP (specified content of DA is 40 mg/ml) and 1 ml of human urine sample without any pretreatment were diluted to 100 ml with buffer respectively and diluted solutions were pipette into each of series of 10 ml volumetric flasks and to this, different known standard concentrations of DA and UA solutions were added and diluted to the mark with pH 7 phosphate buffer.

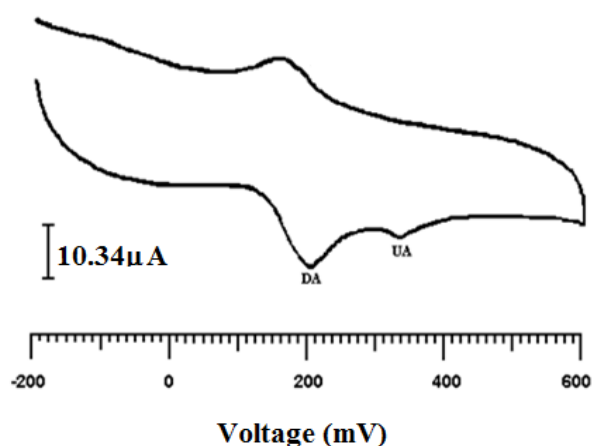


Fig. 15. Typical cyclic voltammogram for the simultaneous determination of 1: 500 dilutions of DA and UA in DA hydrochloride injection USP and healthy human urine sample solution respectively

The cyclic voltammograms were recorded and the peak currents were measured for DA and UA. Fig. 15 shows a typical cyclic voltammogram for the simultaneous determination of DA and UA in DA hydrochloride injection USP and healthy human urine sample solution respectively. The obtained results were shown in Table 1 and the results were consistent well with the certified values, suggesting that the Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode has a good precision and the proposed method can be efficiently applied to the simultaneous determination of DA and UA.

Table 1. Simultaneous determination of DA and UA in injection and human urine mixture sample in 0.2 M PBS (n=5).

Sample no.	DA added(μ M)	UA added(μ M)	DA		UA	
			Found(μ M)	Recovery (%)	Found(μ M)	Recovery (%)
1	0	0	39.45	-	24.22	-
2	10	10	49.34	99.32	34.56	99.31
3	20	20	59.70	99.48	44.23	99.67
4	30	30	68.86	99.89	54.78	99.98
5	40	40	79.36	99.32	65.46	99.23

4. CONCLUSION

The Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode based on grinding has been prepared for the electrochemical determination of dopamine (DA) and uric acid (UA). Results showed that the oxidation peak current of dopamine (DA) and uric acid (UA) was improved at Ni_{0.02}Sn_{0.98}O₂ nanoparticles modified carbon paste electrode. The electrochemical response is diffusion controlled and Quasi reversible and irreversible in nature for DA and UA respectively. A linear concentration range was found to occur from 1×10^{-5} to 1×10^{-3} M. The probable reaction mechanism involved in the oxidation of DA and UA were also proposed. The NSNMCPE was used for the simultaneous determination of DA and UA, the separation of the overlapping voltammograms of dopamine and uric acid at modified electrode in a mixture is successfully carried by using cyclic voltammetric technique. The proposed method was successfully applied for the determination of DA and UA due to its good sensitivity, lower detection limit and ease of preparation of the NSNMCPE allows the development of a highly sensitive voltammetric sensor for the determination of DA and UA.

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