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Full Paper

Nickel Oxide Modified Carbon Paste Electrode for the cyclic voltammetric Detection of L-Tryptophan and Uric acid

M. Shruthi Vishwanath,[1] B. E. Kumara Swamy,[2,*] and K. A. Vishnumurthy[1]

[1]*Dept of Industrial Chemistry, Sir M.V. Science College, Bhadravathi, Karnataka, India*
[2]*Dept of PG studies and research in Industrial Chemistry, Kuvempu University, Jnana Sahyadri, Shankaraghatta, 577451 Shivamogga (D), Karnataka, India*

*Corresponding Author, Tel.: +91-8282-256225

E-Mail: kumaraswamy21@yahoo.com

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Abstract- The selection and development of active material is a challenge. The active sensing materials may be of any kind as whichever acts as a catalyst for sensing a particular analyte or a set of analytes. Nickel oxide (NiO) nanoparticles are formed by using the co-precipitation method and analyzed by XRD, SEM, and EDAX techniques. The NiOMCPE was formed by using a certain amount of graphite powder, silicon oil, and different quantity of (2mg, 4mg, 6mg, and 8mg) NiO nanoparticles and further a bare carbon paste electrode was prepared by using a known amount of graphite powder and silicon oil. The NiOMCPE was used to analyze the parameters like scan rate, pH and concentration of L-tryptophan (TRP), and concentration and scan rate of uric acid (UA). Further, the modified electrodes were used for interference study and simultaneous determination of mixtures of L-tryptophan and uric acid. The same method can also be used for some other bioactive molecules.

Keywords- Nickel oxide nanoparticle; Modified carbon paste electrode; L-Tryptophan; Uric acid

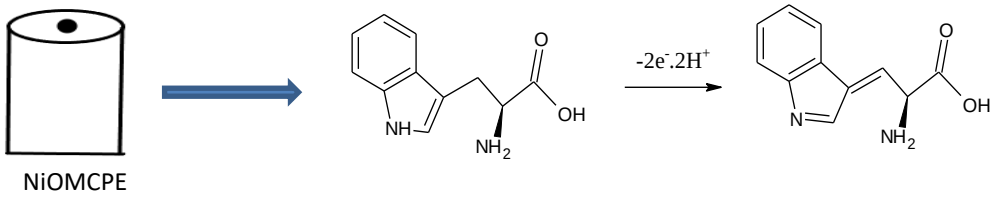
1. INTRODUCTION

Nanoparticles are a powerful weapon against pathogenic viruses. Nanoparticles are emitting electrons and these electrons are attached themselves to the viruses and destroy the surface of the viruses. The surfaces are removed frequently to clean from a number of viruses. Researchers have placed a tiny camera used to observe chemical reactions in real-time [1,2]. Nickel oxide nanoparticles are p-type semiconductors hence they are used in many fields like battery cathodes, gas sensors, and electrochromic films.it is used as a magnetic material in electrochromic display devices. Nickel oxide nanoparticles are better antibacterial agents [3,4].

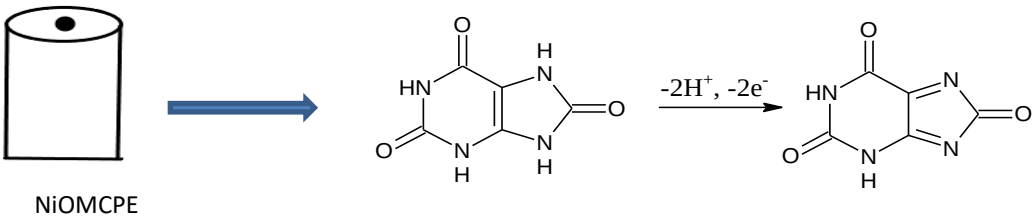
The essential amino acid is L-tryptophan. When a person consumes L-tryptophan the body absorbs and changes into a hormone called serotonin. Serotonin transmits signals between nerve cells and narrow blood vessels. Women take L-tryptophan supplements to ease mood swings due to premenstrual syndrome. It is found in meats like chicken and also found in banana, milk, chocolate, and peanuts. The side effect of L-tryptophan is blurred vision, Nausea, sweating, and head twitching [5-10].

The important antioxidant in human plasma is uric acid. It is also the end product of the degradation of purine nucleosides. A higher level of uric acid causes many diseases like visceral obesity, diabetes, kidney disease, and dyslipidemia [11-15].

Electrochemical techniques have been used for the detection of biomolecules such as LTP and UA because of their high sensitivity, rapid response, simple operation, and low expenses. However, the oxidation potential of these electroactive species is too close to be determined separately by using NiOMCPE. It is an effective modifier used for the simultaneous study of TRP and UA (Scheme 1and 2).



Scheme 1. NiOMCPE and oxidation of L-tryptophan



Scheme 2. NiOMCPE and oxidation of uric acid

In this work, our aim is to synthesize nickel oxide nanoparticles and voltammetric study of synthesized nanoparticles using nickel oxide modified carbon paste electrode. The electrochemical determination of nickel oxide nanoparticles with different techniques such as CV and DPV will be carried out and different parameters like the effect of scan rate, pH, and concentration of L-tryptophan and uric acid were studied. Nickel oxide nanoparticles were also used for the investigation of the individual and simultaneous study of TRP and UA. From voltammetric study the nickel oxide nanoparticle exhibit good electric activity and the rate of reaction are determined by diffusion of the analyte to the surface of electrode are adsorption controlled.

2. EXPERIMENTAL SECTION

2.1. Reagents and instrumentation

Nickel chloride hexahydrate, NaOH, potassium chloride, Potassium ferrocyanide, uric acid, graphite powder, silicon oil are purchased from Himedia. L-tryptophan, Sodium dihydrogen orthophosphate, and disodium hydrogen orthophosphate were purchased from Karnataka fine chemicals. By using deionized water, the aqueous solutions are prepared.

Voltammetric measurements are carried out by using the CH instrument. It contains a three-electrode electrochemical arrangement, which consists of bare carbon paste electrode (BCPE) and NiOMCPE as the working electrode, platinum wire as an auxiliary electrode, and aqueous saturated calomel electrode (SCE) as a reference electrode.

2.2. NiO nanoparticles synthesis

Dissolve nickel chloride hexahydrate in 250ml distilled water and the solution was magnetically stirred for 30 minutes at 45^0C temperature. After NaOH is added dropwise to the solution until the pH reaches 7. The obtained gel is washed with ethanol and distilled water and dried at 50^0C for 10 hours. The obtained compound is calcinated at 500^0C for 1 hour. These obtained nickel oxide nanoparticles are used for further characterization.

$$NiCl_2.6H_2O + H_2O + 2\ NaOH \xrightarrow{\Delta} NiO + 8\ H_2O + 2NaCl$$

2.3. Preparation of BCPE and MCPE

Take a known amount of graphite powder and silicon oil in an agate mortar and grind half an hour a homogeneous paste was formed, then the mixture was packed into a Teflon cavity. In preparation of MCPE different quantities of (2mg, 4mg, 6mg, and 8mg) Nickel oxide nanoparticles were mixed with graphite powder and silicon oil, the mixing and packing procedure was the same as that BCPE.

3. RESULTS AND DISCUSSION

3.1. Characterization of prepared nickel oxide nanoparticles

Figure 1A shows the XRD pattern of nickel oxide nanoparticles. The XRD of the nanoparticle shows a sharp peak which indicates the growth in the crystalline size of the nanoparticle. No extra peaks were found in XRD which indicates the purity of the product is high. The size of the NiO nanoparticles was found to be 17.56 nm using Debye–Scherrer Equation. Figure 1B and Figure 1C show the SEM and EDAX images of the synthesized nanoparticles and confirm the presence of Ni, O, Na, Cl and C in the synthesized nanoparticles [16-20].

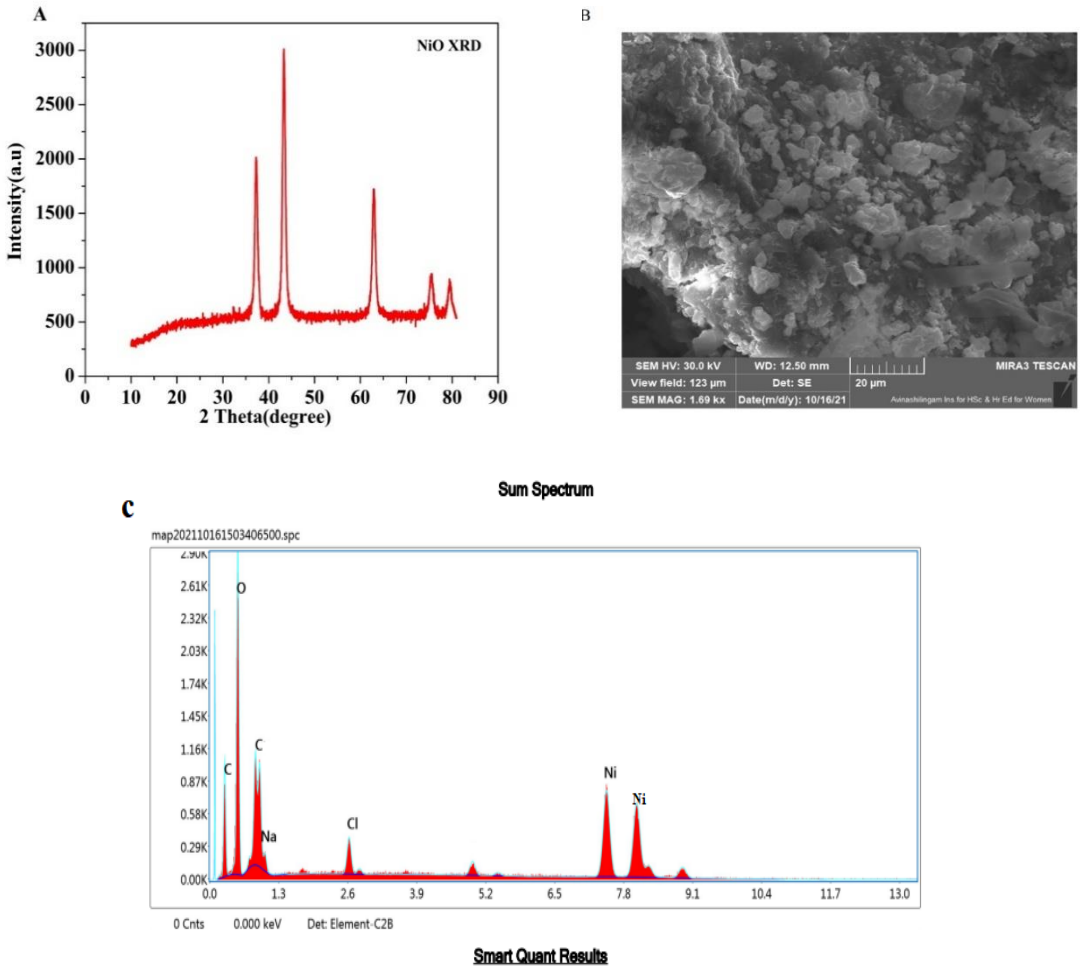


Figure 1. (A), (B) and (C) shows the XRD, SEM and EDAX patterns of nickel oxide nanoparticles

3.2. Comparative analysis for the different quantities of NiOMCPE

The different quantities of synthesized NiO nanoparticles in the carbon paste electrode were studied using 0.2 M phosphate buffer solution (PBS) at pH 7.4 for 25×10^{-4} M L-tryptophan

with a sweep rate of 50 mV/s by CV technique as shown in Figure 2a. Figure 2b shows the graph of anodic peak current (I_{pa}) versus the amount of nickel oxide nanoparticles taken in milligram. The quantity of NiOMCPE increases simultaneously peak current also increases. 8 mg of NiO nanoparticles modified carbon paste electrode shows maximum peak current and it was selected for further analysis.

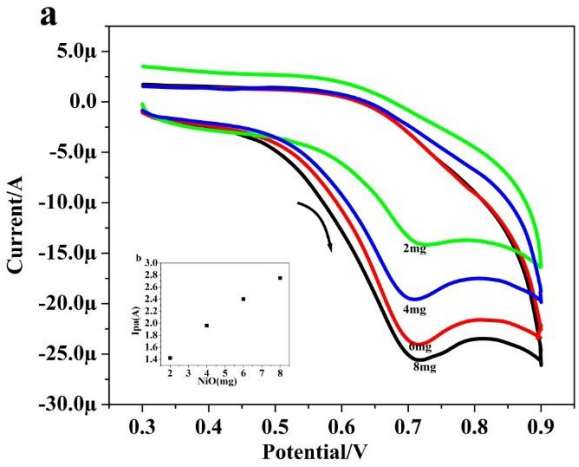


Figure 2. a) CV obtained for different quantity of nickel oxide nanoparticle in the carbon paste electrode was studied in 0.2 M PBS at pH 7.4 for 25×10^{-4} M L-tryptophan with a sweep rate of 50 mV/s; b) Anodic peak current (I_{pa}) versus the amount of nickel oxide nanoparticles taken in milligram

3.3. Determination of surface area of BCPE and NiOMCPE

The electroanalytical behavior of 0.2M $K_4[Fe(CN)_6$ and 1 M KCl at bare and modified carbon paste electrode with sweep rate 50mV/s were studied. Figure 3 represents the redox couple obtained for BCPE (dashed line) and NiOMCPE (solid line). The NiOMCPE shows higher redox peak currents compare to BCPE. The result shows that the modified electrode is more convenient than the bare carbon paste electrode for electrochemical analysis.

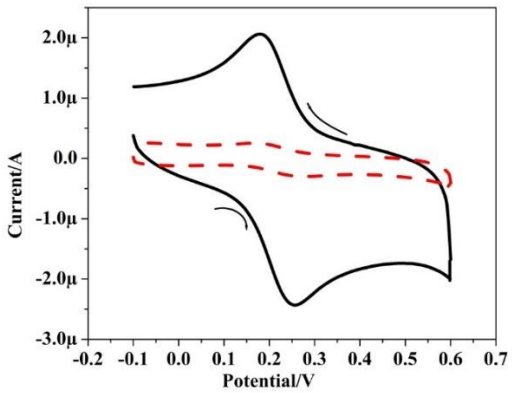


Figure 3. CV of 0.2M $K_4[Fe(CN)_6]$ at BCPE (dashed line) and NiOMCPE (solid line) in presence of 1 M KCl, and a sweep rate of 50m V/s

The area of the bare and modified electrode can be estimated by recording CVs at various sweep rates (0.05-0.5 V/s) in the presence of $K_4[Fe(CN)_6]$ and KCl. The area of BCPE and MCPE is calculated using Randles–Sevcik equation: $Ip = (2.69\times10^5)\, n^{3/2} D^{1/2} v^{1/2} A C$. The surface areas of BCPE and MCPE were found to be 0.027 and 0.034 cm^2 respectively. These results are a good agreement with the larger current found in a modifier.

3.4. Electrocatalytic behavior of L-Tryptophan and uric acid at NiOMCPE.

The electrocatalytic behavior of 25×10^{-4} M L-Tryptophan at BCPE (dashed line) and NiOMCPE (solid line) in 0.2 M phosphate buffer at pH 7.4 as shown in Fig.4. The cyclic voltammogram of NiOMCPE shows an enlargement of the peak current compared to BCPE. Thus, the NiOMCPE showed better electrocatalytic activity than BCPE.

3.5. Effect of pH on L-Tryptophan at NiOMCPE

At different pH the oxidation of 25×10^{-4} M L-tryptophan in PBS and the sweep rate of 50 V/s were investigated over a pH range of 6.2 to7.8 at nickel oxide modified carbon paste electrode. It was observed that the peaks are well defined for a wide pH range (Figure 5a) and if pH is increasing the redox peaks are shifted towards the negative potential. The graph was constructed by plotting the pH versus peak potential (Figure 5b) and the linear regression equation is given as: E_{pa} =0.06825 pH+0.6284 (R^2 = 0.9975). The slope 0.06825 V which is in agreement with the theoretical value of 0.059 V indicates in the chemical reaction the equal number of protons and electrons are involved. The NiOMCPE is established and improved peak current; however physiological pH (7.4) was used for all our electrochemical experiments.

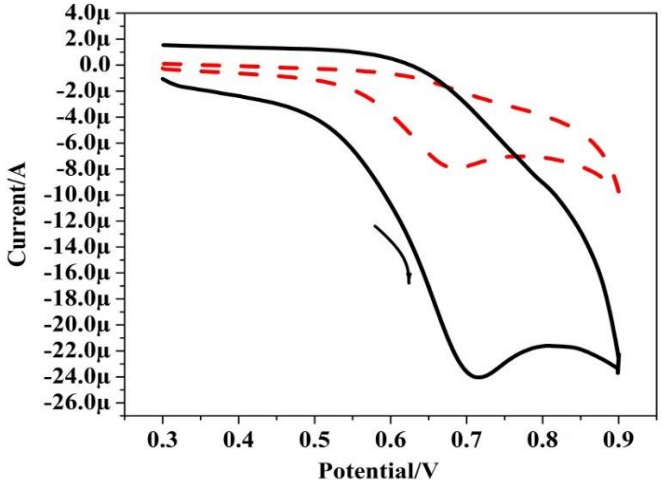


Figure 4. Cyclic voltammograms of 25×10^{-4} M L-tryptophan at BCPE (dashed line) and NiOMCPE (solid line) in 0.2 M phosphate buffer at pH 7.4 and a sweep rate of 50m V/s

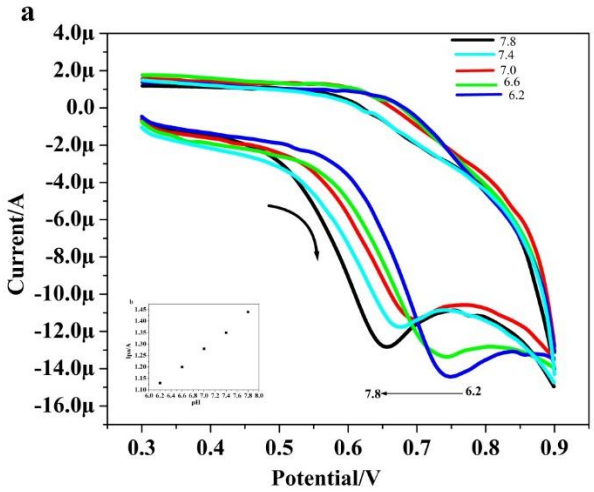


Figure 5. a) Cyclic voltammograms obtained for the 25×10^{-4} M L-tryptophan with a sweep rate of 0.05 V/s at nickel oxide modified carbon paste electrode in various pH (6.2 to7.8) in PBS solutions; b) pH versus the anodic peak potential (E_{pa})

3.6. The effect of scan rate on nickel oxide modified carbon paste electrode

The scan rate effect of 25×10^{-4} M L-tryptophan and 25×10^{-4} M uric acid at NiOMCPE is studied by CV in presence of 0.2M PBS at pH 7.4 by varying sweep rates from 0.05 to 0.5V/s as shown in figure 6a and 6b shows if sweep rate increases anodic peak current also increases. Figure $6a_1$ and $6b_1$ the graph of I_{pa} versus the sweep rate (ν) and figure $6a_2$ and $6b_2$ the graph of log of I_{pa} versus the log of sweep rate (ν) shows a linear relationship with a correlation – coefficient of 0.9869 and 0.9970 for L-Tryptophan and for uric acid 0.9962 and 0.9954 respectively. This indicates the electrode transfer reaction was adsorption controlled.

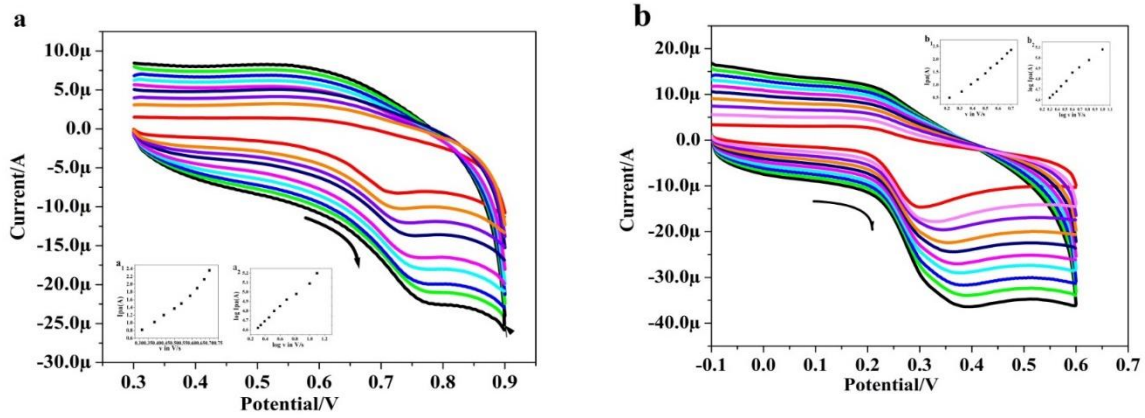


Figure 6. a) Cyclic voltammograms of 25×10^{-4} M L-tryptophan and b) uric acid at NiO MCPE in 0.2 M PBS at sweep rates (0.05 V/s-0.5 V/s); Fig. $6a_1$ and Fig. $6b_1$ Graph of anodic peak current versus the sweep rate. Fig $6a_2$and Fig.$6b_2$ Graph of log of anodic peak current versus log of sweep rate

3.7. The effect of concentration on NiOMCPE

In CV by varying concentrations of 25×10^{-4} M L-tryptophan and uric acid in 0.2 M PBS at a sweep rate of 50 V/s at NiOMCPE as shown in Figures 7a and 7c. The concentration of L-tryptophan from 10 to 50 µM and uric acid from 10 to70 µM increases the anodic peak potential also increases. Figures 7b and 7d show the plots of anodic peak current versus the different concentrations of linear ranges were obtained. It gives an almost straight line and good linearity with a correlation coefficient value found at R2 = 0.9992 and R^2=0.9938 for L-Tryptophan and uric acid respectively. The LOD and LOQ for L-tryptophan are 2.17 and 7.23 µM and uric acid is 7.9 and 26.35 µM respectively [21,22]:

$$LOD=3S/M \quad (1)$$

$$LOQ=10S/M \quad (2)$$

where M is the slope and S is the standard deviation. The detection limit of MCPE for L-tryptophan and uric acid with other reported modified electrodes is presented in Table 1.

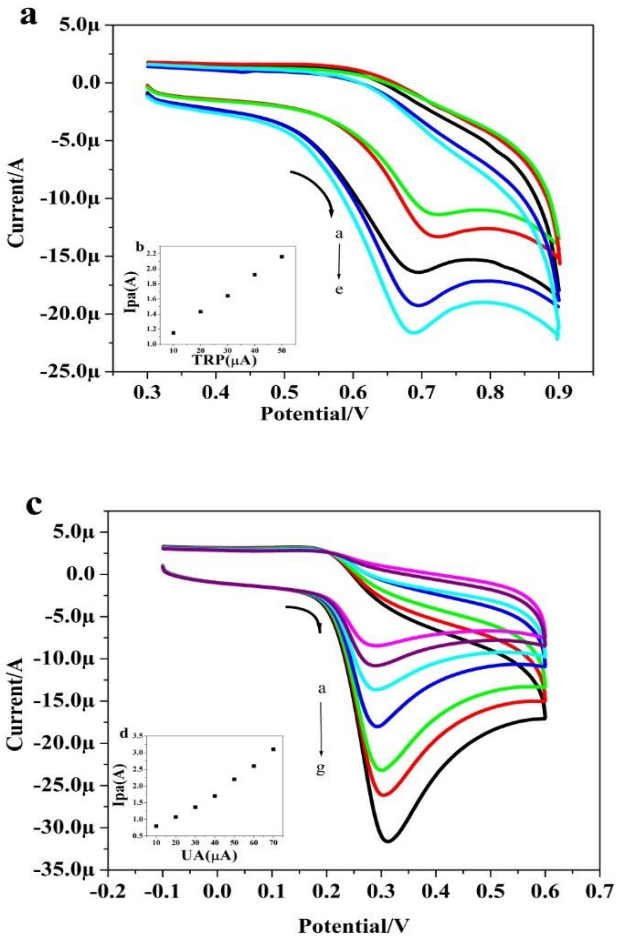


Figure 7. a) Cyclic voltammograms of different concentrations of L-tryptophan and c) uric acid at NiOMCPE in 0.2 M PBS at the sweep rate of 0.05 V/s. Fig.7b and 7d. Graph of I_{pa} *vs.* concentration of L-tryptophan and uric acid

3.8. Simultaneous determination of mixture L-Tryptophan and uric acid at NiOMCPE

The mixture of 25×10^{-4} M L-tryptophan (TRP) and 25×10^{-4} M uric acid (UA) in 0.2 M PBS at bare and modifier as shown in Figure 8a. CVs responses bare shows short current signal and poor selectivity compared to the modifier. MCPE is the ability to separate the oxidation potential of mixed analytes. Figure 8b DPVs response the modified electrode shows a well distinguish peak located at 0.6304 (TRP) and 0.2745 V (UA). Hence, the proposed modifier acts as a good electrochemical sensor for the TRP and UA.

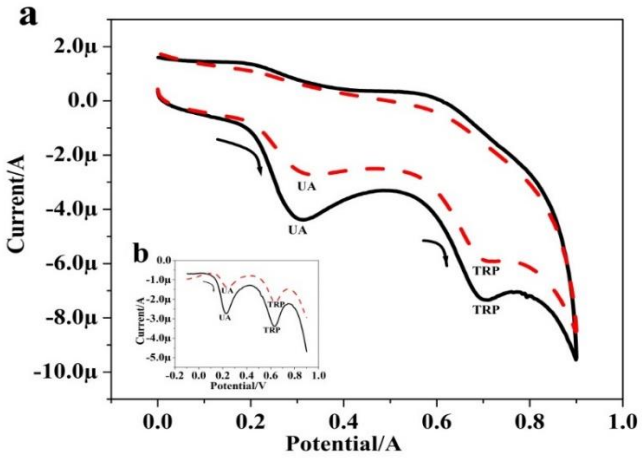


Figure 8. a) CV and b) DPV were obtained for a mixture of TRP and UA (25 µM) at bare (dashed line) and NiOMCPE (solid line) at the sweep rate of 50 mV/s using 0.2 M PBS

3.9. Interference study

An interference study was done by using the DPV technique. In this study by varying the concentration of one species and other kept constant and vice versa.

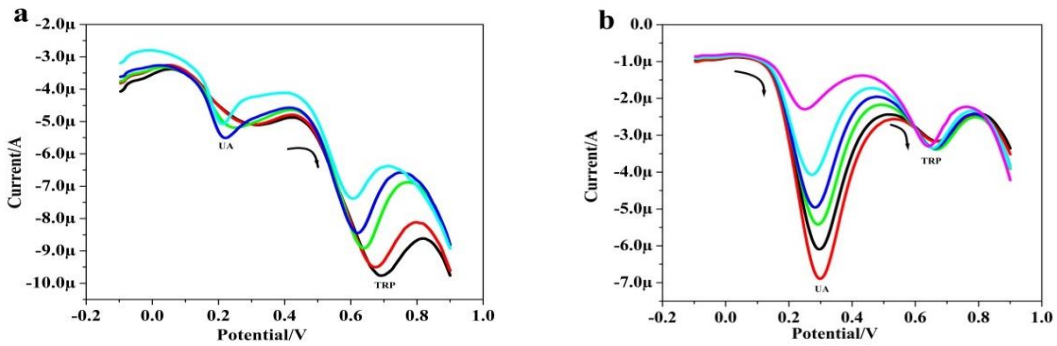


Figure 9. a) DPV of various concentrations of TRP from 10–50 µM in presence of UA and b) various concentrations of UA from 10–60 µM in presence of TRP at NiOMCPE in 0.2 M PBS at a sweep rate of 50 mV/s

Figure 9a shows that the concentration of TRP increases from 10 to 50 μM and UA kept constant. Similarly Figure 9b shows that the concentration of UA was increased from 10 to 60 μM when TRP was kept constant. The DPVs show if anodic peak current increases there are no shifts in the oxidation peak potentials and no change in voltammetric response of UA and TRP.

Table 1. Comparison of LOD of TRP and UA with different electrodes

SI No.	**Working Electrode**	**Electrochemical Technique**	**Detection Limit (μM)**		**Ref.**
			TRP	UA	
1	CNF-CPE	CV	0.1		[23]
2	Poly (Orange CD) FCPE	DPV		0.41	[24]
3	Poly (amido black) MCPE	CV		3.6	[25]
4	Nickel oxide modified CPE	CV	2.17	7.9	This work

4. CONCLUSION

The nickel oxide particles were synthesized by the co-precipitation method and their electrochemical parameters were studied by using L-tryptophan and uric acid. This modified electrode was used for the detection of TRP in presence of phosphate buffer in both cyclic voltammetric and differential pulse voltammetric techniques. The electrode process was by adsorption controlled and the LOD was found to be 7.9 μM. Compared with BCPE and MCPE, the MCPE shows a good electrochemical response towards the detection of TRP and UA along with simultaneous detection TRP and UA. Thus, the proposed method had exceptional sensitivity, selectivity, and interference properties. The developed method has been applied in the field of electroanalytical chemistry and biosensors.

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