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Tungsten oxide (WO₃) Modified Carbon Paste Electrode for Electrochemical Investigation of Dopamine in Presence of Uric Acid and Folic Acid

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Abstract- Present work describes the synthesized and characterization of tungsten oxide nanoparticles (WO₃NPs) was prepared by using tungsten carbide (WC). The prepared material was characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM) and infrared spectroscopy (IR). The prepared WO₃NPs was used as the modifier for the preparation of carbon past electrode (WO₃NPs/MCPE). The fabricated WO₃NPs/MCPE exhibits an excellent electrocatalytic activity towards the dopamine (DA) in the presence of uric acid (UA) and folic acid (FA) in 0.2M phosphate buffer solution (PBS) of pH 7.4 by cyclic voltammetric (CV) and differential pulse voltammetric techniques (DPV). From the effect of scan rate, concentration and pH of the electrode phenomenon was confirmed to be adsorption-controlled process. The lower detection limit of dopamine was 0.58 μM, and the simultaneous analysis shows a good result with peak to peak separation between dopamine and other two analytes uric acid and folic acid by DPV techniques.

1. INTRODUCTION

Tungsten carbide (WC) was used originally for the preparation of tungsten oxide (WO_3). WC is a good oxidation behavior, during milling and storage is of interest in the powder dispensation of tungsten solid alloys and hard metals and therefore this study has concentrated on the oxidation of pure WC at low temperatures (<5OO C) in dry and humid atmospheres. In addition the influence of water which is occasionally used as a milling fluid has been investigated by studying the oxidation behavior of WC in water. WO_3 is the most thermodynamically stable oxide at low temperature and atmospheric pressures it plays an important role as an electrochromic and a catalytically active material. It is a transition metal oxide and small energy band gap between 2.4 to 2.8 eV [1-6]. The key properties of these granular materials are morphology, crystalline structure and chemical purity. Due to the high surface area, the synthesis of WO_3 with nanoplatelet morphology was interested. The main application of WO_3 is photocatalysis and gas sensors [7]. WO_3 was modified with CPE and used as an electrochemical sensor for the detection of dopamine (DA), uric acid (UA), folic acid (FA), these are the one of the essential catecholamine neurotransmitter associated with proper functioning of several organic such as the brain, heart and suprarenal glands [8]. Changes in the concentration of DA may lead to serious diseases such as epilepsy, Schizophrenia and Parkinson's. The level of DA in the body is an important factor in human behavior. Normal levels of DA in the brain result in regular movements, where as higher levels accompany feelings of pleasure and reward and it possesses very strong electrochemical activity by giving dopaquinone as oxidation product. In the human body UA act as a primary product of purine metabolism and a major nitrogenous compound in the urine. In a healthy human being, the typical concentration of UA (2, 6, 8-trihydroxypurine) in urine is around 2 mM and in the blood is in between 120 μM to 450 μM ranges [9, 10]. High level UA in the blood, its abnormality in human body leads to many disorders like Lesch–Nyhan syndrome, hyperuricaemia, cardiovascular disease and multiple sclerosis problems. Many epidemiological studies have suggested that elevated serum UA is also a risk factor for cardiovascular disease [11, 12]. FA is a water-soluble vitamin-B that helps us to produce up the healthy cells. The deficiency causes failure to make the purines and thymine required for DNA synthesis and many studies suggests that diminished foliate status is associated with enhanced carcinogenesis. FA is a potential agent in preventing the growth of cancer cells by free radical scavenging and antioxidant property [13]. There are so many research reports are there for the determination of FA such as, liquid chromatography [14], high performance liquid chromatography [15,16], flow-injection Chemiluminometry [17]. DA, UA and FA are compounds of great biomedical interest, playing a potential role in human metabolism.

In this report, The $WO_3NPs/MCPE$ exhibits enhancement of current response with reduction of over potential for the investigation of DA at pH.7.4 in 0.2 M phosphate buffer

solution (PBS) and electrocatalytic currents increases linearly with increase of DA concentrations and the detection limit was found to be 0.58μM. The fabricated electrode was employed for the electroanalysis of DA in presence of UA and FA at physiological pH.

2. EXPERIMENTAL

2.1. Reagents

The chemicals tungsten carbide purchased from sigma Aldrich, dopamine hydrochloride, Uric acid, Folic acid, sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4) and silicon oil purchased from Himedia chemicals and graphite powder was from Merck chemicals. All other chemicals were of analytical grade.

2.2. Apparatus

Voltammetric measurements were performed with a model 660c (CH instruments). A conventional three electrode cell was used with a reference saturated calomel electrode (SCE), counter electrode as a platinum wire and bare or WO_3NPs/MCPE as working electrodes. The structure of prepared WO_3NPs was studied by XRD using a (Model D8 Advance, Bruker) with a Cu- Kα1 X-ray radiation (λ=0.15406 nm) diffractometer. The morphological structure of the synthesis WO_3NPs was studied using an H-7600(HITACHI) Transmission electron microscopy (TEM) and VEGA3 TESCAN Scanning electron microscopy (SEM). IR absorption spectra are recorded in IR SPECTRUM 1000 PERKIN ELMER spectrometer.

2.3. Preparation of WO_3NPs

Tungsten carbide (WC) was purchased from Sigma Aldrich. 3 g of WC was calcined in air at 600 ^{o}C for 6 hr at both heating and cooling rate of 5 ^{o}C/mins to obtain WO_3NPs.

2.4. Preparation of the bare and MCPEs

The bare CPE was prepared by hand mixing of 80% graphite powder with 20% silicon oil in an agate mortar until a homogenous paste was obtained. The paste was then tightly packed into the homemade cavity of a teflon tube of 3 mm internal diameter and smoothed on a tissue paper till the surface become uniform. The modified carbon paste electrode (MCPE) was prepared by adding 6 mg WO_3NPs hybrid nanoparticles to above mentioned graphite powder and silicon oil mixture.
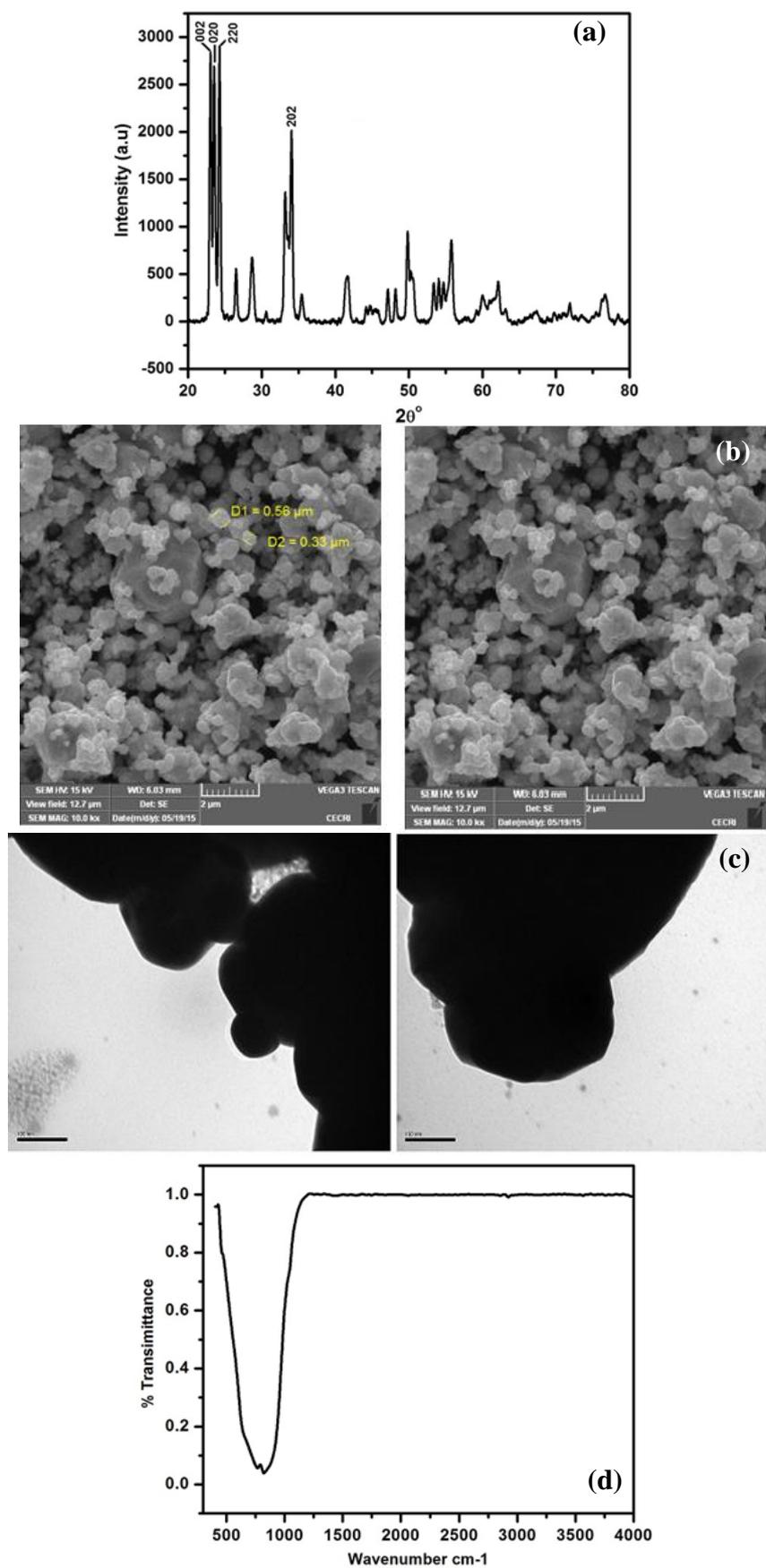
Fig. 1. (**a**)X-ray diffraction pattern of the prepared WO$_3$NPs; (**b**) SEM image of prepared WO$_3$NPs; (**c**)TEM image of WO$_3$NPs; (**d**) IR spectra of prepared WO$_3$NPs

3. RESULTS AND DISCUSSION

3.1. Characterization of prepared WO₃NPs

The WO₃NPs where characterized by various technique. XRD patterns of Fig. 1a shows the peak corresponding to 002, 020, 220 and 202 planes at $2\theta=23.10$, 23.48, 24.29 and 34.10 respectively. This peaks matched with standard pattern of a monoclinic WO₃ (JCPDS No. 43-1035) [18]. Using Debye Scherer's equation, the size of WO₃ can be determined. The obtained average particle size of WO₃NPs is 35 nm.

The surface morphology of the samples obtained SEM and TEM images are shown in figure. The SEM and TEM images clearly show different morphologies and sizes for WO₃. Flake shaped structure was observed for WO₃ in the SEM image in Fig.1b and in the corresponding TEM image for the same sample in Fig. 1c Upon close examination, the particles in the TEM image were observed to nanoparticles WO₃ were well dispersed. [19]

Fig.1d shows the IR spectra of WO₃ calcined at 500° C. The broad peaks of the (W-O-W) triplet (500–900 cm^{-1}) assigned to stretching vibration of WO₃. The presences of these peaks indicate the formation of WO₃ particles. [20]
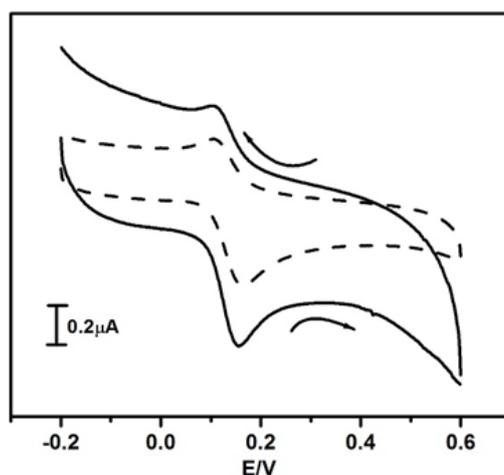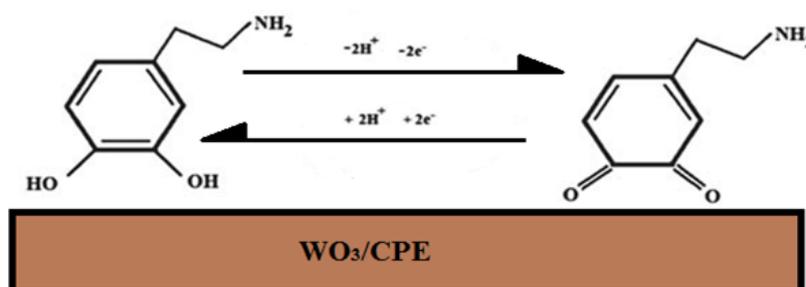

Fig. 2. Cyclic voltammograms of 2×10^{-4} M DA in 0.2 M PBS of pH 7.4 at bare CPE (dashed line) and WO₃NPs/MCPE (solid line)

Scheme 1. Electrocatalytic oxidation of DA at the surface of WO₃NPs on a CPE

3.2. The electrochemical response of DA at the bare CPE and WO₃ NPs /MCPE

Fig. 2 showed the cyclic voltammograms of 2×10^{-4} M DA at BCPE (dashed line) and $WO_3NPs/MCPE$ (solid line) at the sweep rate of 50 mVs^{-1}. DA is an easily oxidizable catecholamine, showed poor sensitivity and reproducibility at BCPE in 0.2 M PBS of pH 7.4. The $WO_3NPs/MCPE$ shows good enhancement in the anodic peak current (I_{pa}) compared to BCPE, among that $WO_3NPs/MCPE$ illustrate very significant enhancement in the peak current with minimization in over potential compared to bare electrode. The differences in peak potential (ΔE_p) were found to be at 0.059 V and 0.051 V for BCPE and $WO_3NPs/MCPE$ respectively. The obtained result confirms that, the $WO_3NPs/MCPE$ exhibit good electrochemical sensors on DA [21]. The schematic illustration of the electrocatalytic activity of DA on the $WO_3NPs/MCPE$ is shown in Scheme 1.

3.3. Effect of pH on DA at the WO₃NPs/MCPE

The electrochemical response of DA at $WO_3NPs/MCPE$ is generally pH dependent. The effect of pH on the determination of DA in PBS at the $WO_3NPs/MCPE$ was carefully investigated in the pH range of 5.8 to 7.8. In Fig. 3, graph (a) anodic peak current (I_{pa}) versus the pH of the solution shows the DA increases with increasing pH values until the pH reaches 7.4, the anodic peak current then decreases with further increases in the pH. The maximum anodic peak current occurred at pH 7.4. Therefore, pH 7.4 was selected for all subsequent electrochemical DA analyses. In graph (b), anodic peak potential (E_{pa}) versus the pH of the solution, the formal potential (E^0) of DA decreased with an increase in the pH value. A linear regression equations obtained were E^0 (V)$=-0.0451$ pH + 0.4834 (n=6, γ=0.9848) for the $WO_3NPs/MCPE$.
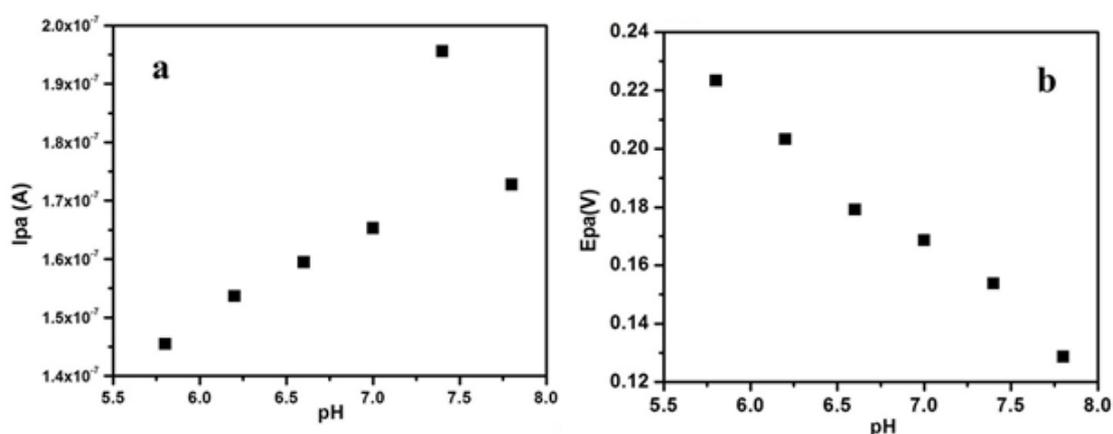

Fig. 3. Graph shows the dependences of the DA oxidation peak potential (a) and for formal oxidation peak current (b) on the PBS solution pH with a scanning rate of 50 mVs^{-1}

The slopes were 0.0451V/pH respectively, which were nearly theoretical value of −0.0576 V/pH. The results indicate that two electron transfer accompanied by two-proton transfer occurred, which were identical to the results reported [22,23].

3.4. Effect of scan rate on DA at the WO$_3$NPs/MCPE

The scan rate effect of 2×10^{-4} M DA in 0.2 M PBS (pH 7.4) was studied at WO$_3$NPs/MCPE as shown in Fig. 4, there is an increase in the redox peak current with increases in scan rate from 50 to 400 mVs^{-1}. The graph of anodic peak current (I_{pa}) versus scan rate (ν) in Fig.4 (inset) shows good linearity with linear regression equation: I_{pa} (μA)$=6.2469\times10^{-7}+8.7778\times10^{-9}$ ν (mV/s) and their correlation coefficient (r^2) were found to be 0.9995. From this study shows electrode reaction was adsorption controlled process.

According to an equation previously reported [24], Eq. (1) determining the value of k^0 from experimental ΔE_p values was valid approximation of such curves for $\Delta E_p>10$ mV. The values of k° for the DA were determined from the experimental ΔE_p values, the data are in Table 1. The values of k^0 indicate that strong adsorptions of reactants and products are involved. Here, the k^0 is the heterogeneous rate constant, and ΔE_p is the potential difference between the anodic and cathodic peak potentials. The heterogeneous rate constant (k^0) was estimated using Eq. (1). The value of k^0 obtained at the scan rate of 50mVs^{-1} for the MCPE prepared with WO$_3$NPs/MCPE exhibits a larger heterogeneous rate constant compared with those determined in other scan-rate-variation studies. The calculated data are tabulated in Table 1.
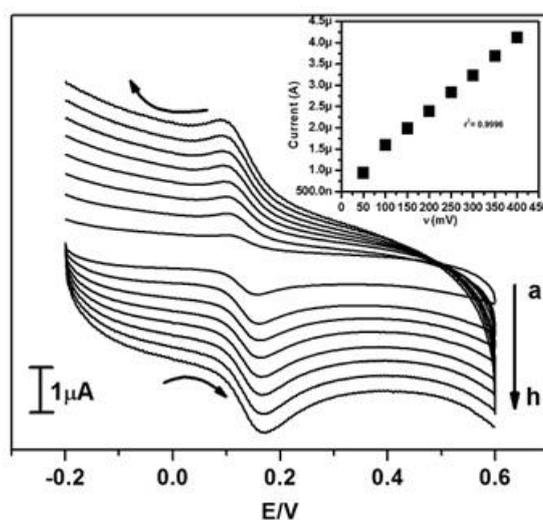
$$\Delta E_p=201.39 \log (\nu/k^0)-301.78 \tag{1}$$

Fig. 4. Cyclic voltammograms of WO$_3$NPs/MCPE in PBS solution pH 7.4 with different scan rate DA (a) 50 mVs^{-1}, (b) 100 mVs^{-1}, (c) 150 mVs^{-1}, (d) 200 mVs^{-1}, (e) 250 mVs^{-1}, (f) 300 mVs^{-1}, (g) 350 mVs^{-1} and (h) 400 mVs^{-1} (Inset) Graph of I_{pa} versus scan rate of DA

Table 1. Electrochemical parameters of DA at different scan rates

$\nu(mV\ s^{-1})$	$\Delta E_p(mV)$	$k^0(s^{-1})$
50	59	0.816
100	57	0.604
150	65	0.441
200	64	0.327
250	72	0.287
300	75	0.247
350	71	0.202
400	82	0.201

3.5. Concentration effect of DA at the WO₃NPs/MCPE

The concentration effect of DA from 2×10^{-4} to 11×10^{-4} at WO₃NPs/MCPE in 0.2 M PBS of pH 7.4 at the scan rate 50mVs^{-1} was studied. Both redox peak current increases with increase in the concentration of DA and the anodic peak currents shift slightly towards negative side as in the Fig.5. The graph of I_{pa} versus concentration of DA in Fig.5 (inset) shows there is an increase in peak current with increase in the concentration and the linear regression equation was: I_{pa} (µA)=1.1619×10^{-7}+5.1543×10^{-8} C (M/L) for anodic peak current and their correlation coefficient was found to be 0.9985.
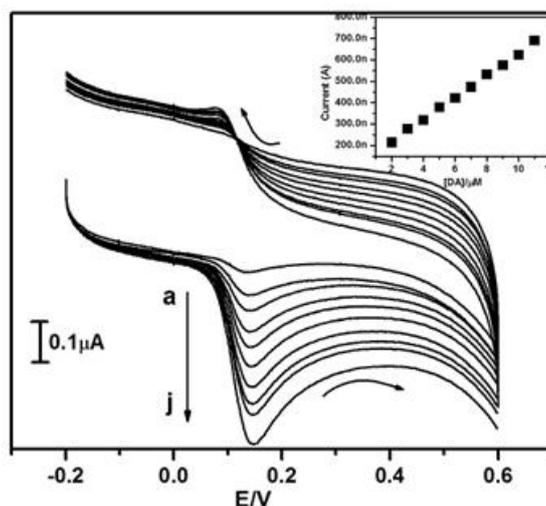

Fig. 5. Cyclic voltammograms of WO₃NPs/MCPE in 0.2 M PBS solution of pH 7.4 with different concentration DA (a) 2×10^{-4}, (b) 3×10^{-4}, (c) 4×10^{-4}, (d) 5×10^{-4}, (e) 6×10^{-4}, (f) 7×10^{-4}, (g) 8×10^{-4}, (h) 9×10^{-4}, (i) 10×10^{-4} and (j) 11×10^{-4}. (Inset) Graph of Ipa versus concentration of DA

3.6. Interference study of the WO₃NPs/MCPE

The interference investigation was performed in the mixture of samples containing DA, UA and FA at the WO₃NPs/MCPE.
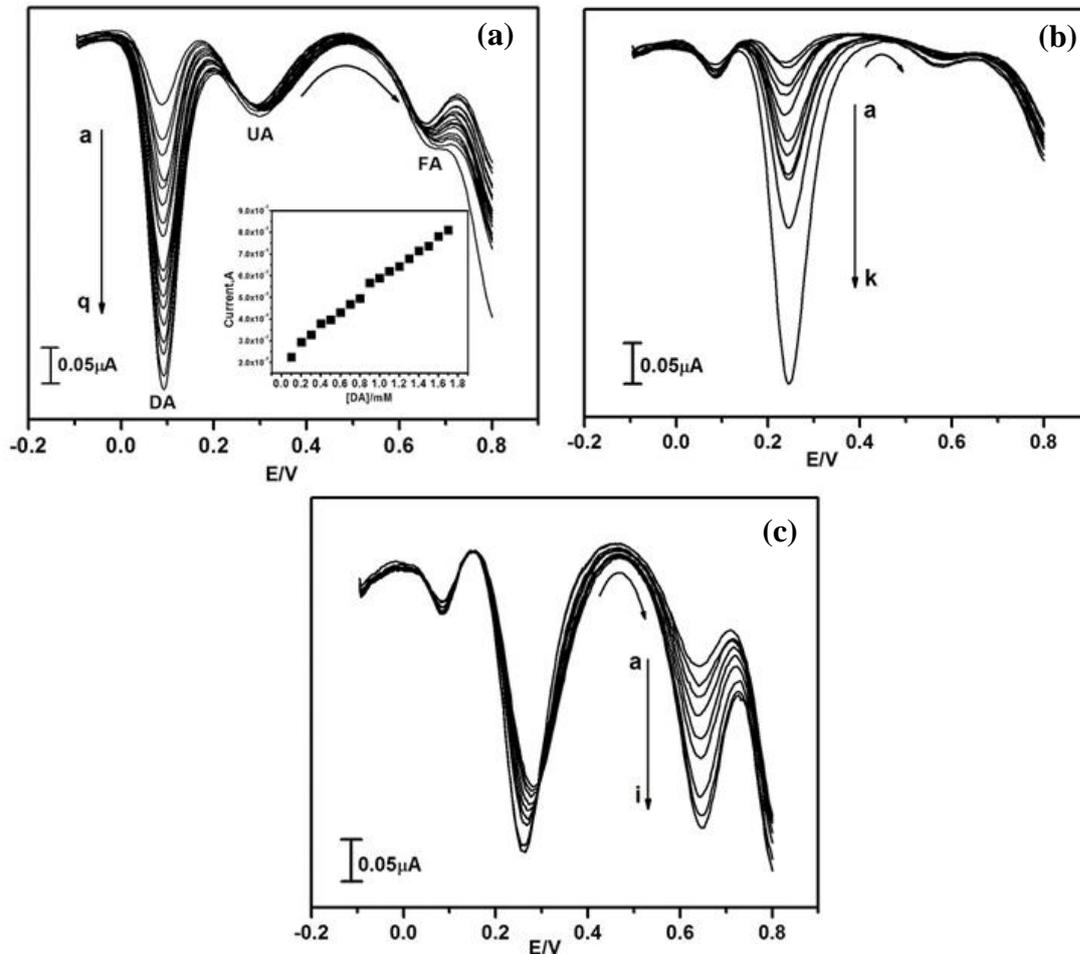

Fig. 6. (a) Differential pulse voltammograms of (a) 0.1 μM, (b) 0.2 μM, (c) 0.3 μM, (d) 0.4 μM, (e) 0.5 μM, (f) 0.6 μM, (g) 0.7 μM,(h) 0.8 μM, (i) 0.9 μM, (j) 1.0 μM, (k) 1.1 μM, (l) 1.2 μM, (m) 1.3 μM, (n) 1.4 μM, (o) 1.5 μM, (p) 1.6 μM and (q) 1.7 μM DA in 0.2 M PBS of pH 7.4 in the presence of 20μM UA and 30 μM FA at WO₃NPs/MCPE with the scan rate of 50 mV s^{-1}; **(b)** Differential pulse voltammograms of (a) 20 μM (b) 30 μM (c) 40μM, (d) 50 μM, (e) 60 μM, (f) 70 μM, (g) 80 μM,(h) 90μM, (i) 100 μM, (j) 110 μM, and (k) 120 μM UA in 0.2 M PBS of pH 7.4 in the presence of 0.1 μM DA and 30 μM FA at WO₃NPs/MCPE with the scan rate of 50 mV s^{-1}; **(c)** Differential pulse voltammograms of (a) 30 μM, (b) 40 μM, (c) 50μM, (d) 60 μM, (e) 70 μM, (f) 80 μM, (g) 90 μM, (h) 100μM and (i) 110 μM FA in 0.2 M PBS of pH 7.4 in the presence of 0.1 μM DA and 20 μM UA at WO₃NPs/MCPE with the scan rate of 50 mV s^{-1}

The concentration of one species changed, whereas the others kept constant. From the Fig.6a it can be seen that the peak current of DA was proportional to its concentration, which was increased from 0.1 to 1.7 µM when keeping the concentration of UA 20 µM and FA 30 µM. There were no change in the peak current and peak potential occurred for UA and FA. Similarly in Fig. 6b and 6c self explains the concentration effect of UA from 20 to 120 µM and FA from 30 to 110 µM respectively. These results shows that the DA, UA and FA were exist independently in their mixtures of samples. To study the effect of concentration of DA, DPV technique was used [25].

Table 2. Comparisons of the lower detection limit of $WO_3NPs/MCPE$ for DA with different modified electrodes

Electrodes	Detection limit (mol/L)	Techniques	Ref.
Nanostructured polyaniline/ tungstophosphoric acid CPE	3.0×10^{-7}	DPV	[28]
Carbon nanotubes paste electrode modified with ferrocenedicarboxylic Acid	1.1×10^{-6}	DPV	[29]
Poly (DL- serine/SiO2)/CPE	1.1×10^{-7}	DPV	[30]
Poly(brilliant blue) modified CPE	6.7×10^{-7}	CV	[31]
Bicopper complex modified GCE	1.4×10^{-6}	DPV	[32]
ZnO NWs/ITO	6.4×10^{-6}	CV	[33]
Banana/MWCNTs/MCPE	2.09×10^{-6}	DPV	[34]
Ag NPs/CNTs	0.3×10^{-6}	DPV	[35]
MWCCE	1.5×10^{-6}	CV	[36]
CCE/ferrocene	0.45×10^{-6}	SWV	[37]
WO_3/MCPE	5.8×10^{-7}	DPV	Present work

The concentration of DA was varied from 0.1 to 1.7µM. (inset) Fig.6a shows that the graph of anodic peak current verses concentration of DA shows linear relationships ranges from 0.1 to 1.7µM with the linear regression equation $I_{pa}(\mu A)=2.2113\times10^{-7}+3.5304\times10^{-7}$ C (µM/L) respectively. The correlation coefficient was 0.9988. The detection limit for DA in

the lower range region was found to be 0.58 µM. The detection limit was calculated by using the formulas, LOD=3S/M. Where S is the standard deviation and M is slope obtained from the graph [26]. The LOD obtained from the DA concentration studies from DPV technique was compared to various reported elsewhere in the Table 2.

$$LOD=3S/M \quad\quad\quad (2)$$

3.7. Stability and reproducibility of the WO₃NPs/MCPE

The reproducibility of the conventional method for determining DA was examined in the presence of PBS (pH.7.4) containing 0.1 µM DA by 15 cycle measurements as shown in the Fig.7 the consequence led to the good reproducibility. After each determination the modified electrode was washed with PBS and scanned using cyclic voltammetry in the blank PBS until the redox response wave of DA disappeared at 50 mVs⁻¹ in the potential range of −0.2 V to 0.6 V. After 6 days exposure of the modified electrode in air, it was found that the electrochemical activity of the WO₃NPs/MCPE over the determination of DA remained almost the same, which indicated the good reproducibility and stability of the WO₃NPs/MCPE [27].
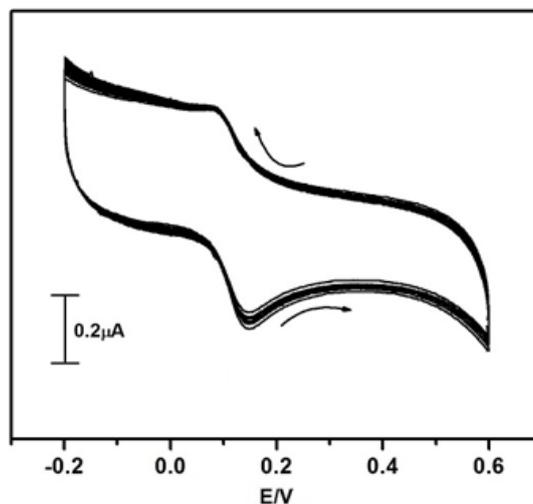

Fig. 7. Cyclic voltammogram of 0.1 µM DA in the presence of PBS (pH 7.4), at a scan rate of 50 mV s⁻¹ at WO₃NPs/MCPE for 30 cycle measurements

4. CONCLUSION

The prepared WO₃NPs/MCPE was characterized by XRD, SEM, TEM and IR spectra. The WO₃NPs/MCPE for the electrochemical determination of DA in presence of PBS pH 7.4 at the scan rate of 50 mVs⁻¹. WO₃NPs/MCPE exhibits remarkable electrocatalytic effects on oxidation of DA when compared to BCPE. From the scan rate study of DA on

$WO_3NPs/MCPE$ was found to be adsorption controlled electrode process. The concentration of DA on $WO_3NPs/MCPE$ were studied using CV and DPV techniques and the LOD were calculated and obtained good result compared to some of the literatures. $WO_3NPs/MCPE$ showed good stability and reproducibility towards the DA and also effect of interferences (DA, UA and FA) was studied by DPV technique. From the obtained result it is expected that $WO_3NPs/MCPE$, with its high electrocatalytic behavior find good applications in the field of electroanalytical chemistry.

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