Anal. Bioanal. Electrochem., Vol. 12, No. 4, 2020, 553-568

Analytical &
Bioanalytical
Electrochemistry

2020 by CEE
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Full Paper

Poly(Niacin) Based Carbon Nanotube Sensor for the Sensitive and Selective Voltammetric Detection of Vanillin with Caffeine

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Received: 20 March 2020 / Received in revised form: 13 April 2020 /
Accepted: 17 April 2020 / Published online: 30 April 2020

Abstract-In the current work, a novel sensor was developed for the analysis of Vanillin (VN) by electrochemical polymerization of Niacin over the surface of carbon nanotube paste electrode. The features of electrode surface was studied using Field Emission Scanning Electron Microscopy (FE–SEM) images. Sweep rate variation study was conducted in the optimum pH (pH 7.0) for the evaluation of number of electrons involved in the electrochemical reaction and to investigate the mode of mass transfer phenomena. This investigation reveals that the electrode undergoes adsorption controlled mass transfer process. Based on the data obtained from the measurements the oxidation mechanism of VN was proposed. The prepared sensor was also applied for the simultaneous detection of VN and Caffeine (CF). Quantitative determination of VN was accomplished by cyclic voltammetric (CV) method. The corresponding value of limit of detection (LOD) and limit of quantification (LOQ) of VN was found to be 10.1×10^{-7} M and 3.3×10^{-6} M, respectively. In addition, the applicability of the proposed method was checked with the detection of VN in real sample with good recovery data.

Keywords- Cyclic voltammetry; Vanillin; Poly(Niacin); Real sample analysis

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1. INTRODUCTION

Vanillin (VN) (4-hydroxy-3-methoxybenzaldehyde) (Fig. 1A) is recognized as one of the most accepted flavouring component naturally extracted from vanilla bean [1,2]. It is most extensively used as an aromatic agent in perfumes, candles, air fresheners, cosmetics and incenses and also used as a flavouring agent in beverages, foodstuffs, confectionery and medicines [3–5]. VN also possess health benefits such as preventing heart disease fatality, and sickle cell anaemia [6, 7]. Conversely, its undue intake can cause adverse health effects including nausea, headache, irritation to skin, vomiting, as well as it damages kidney, liver [8–10]. Hence, FDA has made regulation that the concentration of VN in foodstuffs should be less than 70 mg/kg [11]. However synthetic VN is inexpensive and extensively produced, the demand for superior quality natural vanillin is increasing because of food safety concerns [12,13]. Therefore, with the intension of food safety and quality, it is of great interest to develop and promote the potential approach for effortless, sensitive and economical determination of VN quantity in food product.

Numerous analytical techniques have been already reported in the literature for detecting VN such as spectroscopy [14], chemiluminescence [15], liquid chromatography-mass spectrometry [16], capillary electrophoresis [17], gas chromatography-mass spectrometry [18], High performance liquid chromatography [19] and various chemically modified electrodes [20–23]. Even though these techniques exhibited satisfactory outcome, they have suffered from some defects, such as expensive analysis cost, measurements require more time, and it requires convoluted sample per-treatment .

In spite of these benefits, the electro-oxidation reaction of VN takes place at unmodified electrode surface is less sensitive and is inadequate for selective determination [24]. Since VN is a phenolic moiety which can generate phenoxy radical which readily undergo polymerization and inactivates the surface of the electrode [25]. Therefore, in order to overcome from this predicament the bare electrode surface has to be modified with some adequate surfactant molecules, metal nanoparticles, or with polymers. Because these possesses intriguing structures which boost the sensitivity of the electrode [26–28]. Nowadays polymer modified electrodes have fascinated the researchers for the analysis of bioactive molecules because these seizes elevated conductive property, high stability, economical and the electrode surface can be easily renewable [29,30].

The commonly using technique for the formation of polymeric film at the surface of bare electrode is electropolymerization. By the application of this method the analyst can control the thickness of the polymer film by optimizing the number scanning segments and the potential window [31]. Poly(niacin), is an interesting polymer because it is commercially available, the electron conductivity is high, highly stable and can strongly adhered at the electrode surface [32]. The flavouring agents VN and CF are using in most of the bakery food products in low concentration. If the concentration of these moieties increased, it causes toxicity to the consumer. So in the present analysis, Poly (niacin) modified carbon nanotube paste electrode (PNMCNTPE) was prepared for the determination of VN and it was simultaneously detected with CF (Fig. 1B). The surface properties of the electrode was studied using FE-SEM imagery. This proposed method was successfully adopted for the quantification of VN in real sample.

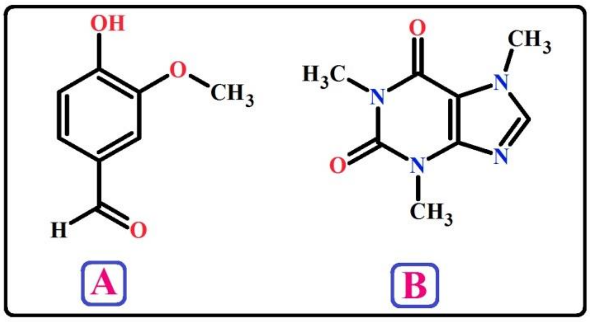


Fig. 1. Chemical structure of **A)** Vanillin **B)** Caffeine

2. MATERIALS AND METHODS

2.1. Reagents and chemicals

VN was procured from Medilise chemicals, Kerala. CF and Niacin were purchased from Molychem, India. Multi walled carbon nanotubes (MWCNT) having external diameter 30–50 nm and length 10-30 µm was obtained from Sisco Research Laboratory Pvt. Ltd. Maharashtra. All the reagents and chemicals used for this analysis were of analytical grade quality and were utilized as obtained without taking to further purification process. Phosphate buffer solution (PBS) was prepared by dissolving calculated quantity of monobasic and dibasic sodium phosphate in distilled water. Potassium chloride (KCl) and $K_4[Fe(CN)_6]$ (Potassium ferrocyanide) were procured from Sigma-Aldrich, India. All the solutions used for this analysis were prepared using distilled water.

2.2. Instrumentation

All the electrochemical measurements were performed using the electrochemical workstation of model CHI-6038E (CH Instruments, USA) connected to a computer for recording the response and storing the data. This instrument is equipped with a conventional three electrode cell in which carbon nanotube paste electrode (bare and PNMCNTPE) as a working electrode, platinum wire served as an auxiliary electrode and saturated calomel electrode as a reference electrode. All the electrochemical measurements were carried out at room temperature.

2.3. Preparation of bare and PNMCNTPE

The carbon nanotube paste was prepared by hand mixing MWCNT and silicone oil in the ratio 60:40 and finely grounded using agate mortar and pestle for about 20 minutes to acquire a homogeneous paste. Then the cavity (3 mm internal diameter) of the Teflon tube was suffused with prepared paste and rubbed over the tissue paper to get a smooth surface. The electrical contact was done through copper wire by inserting at the end of the Teflon tube. Thus the prepared sensor was utilized as a bare carbon nanotube paste electrode (BCNTPE).

The PNMCNTPE was constructed through electropolymerization technique. Fig. 2 demonstrates the cyclic voltammogram generated for the formation of poly(niacin) film on the BCNTPE surface. The electrode was cycled for 20 segments in a PBS containing 1 mM Niacin over the potential range -1.0 to +1.8 V at a sweep rate of 0.1 V/s. During the continuous potential scanning, the current response goes on increases, signifying the formation of polymeric film and the enhancement in the conductivity of the electrode surface. After completion of electropolymerization, the electrode surface was cleansed with distilled water to remove the physically adsorbed particles.

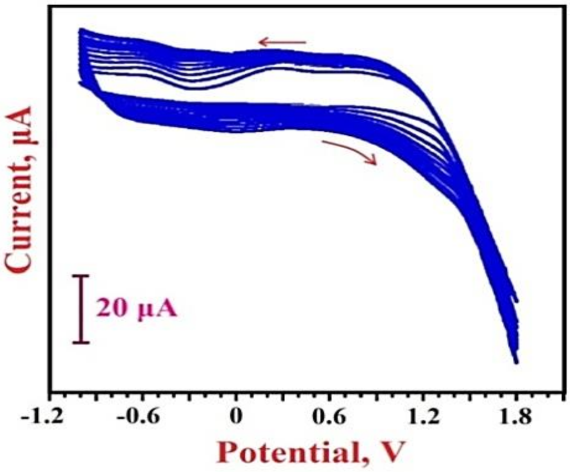


Fig. 2. Cyclic voltammogram generated for electropolymerization of 1 mM Niacin on BCNTPE for 20 segments

2.4. Real sample solution preparation

By utilizing the quantity of VN mentioned in the commercial sample, the amount of sample required for the preparation of solution with known concentration was calculated. Then it was prepared by the dilution of estimated quantity of real sample in deionised water.

3. RESULTS AND DISCUSSION

3.1. Evaluation of electroactive surface area

In order to evaluate the electroactive surface area of the BCNTPE and PNMCNTPE, the cyclic voltammetric response of 1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl was recorded. Fig. 3 displays the CV behaviour of bare and modified electrode, in which it can be clearly observed that the current response was high at PNMCNTPE, whereas at BCNTPE the current response was very less. This activity is probably due to the enhancement in the electroactive surface area of the modified electrode. The Randles Sevcik equation (equation 1) was applied to check the surface area of the electrode [33,34].

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C \quad (1)$$

In the above equation, Ip is the peak current, n represents the number of transferred electrons over redox reaction, A symbolizes the electroactive surface area, D signifies the diffusion co-efficient of molecules present in the solution, ν denotes the sweep rate of the potential scan, and C is the concentration of $K_4[Fe(CN)_6]$ solution. By applying the subsequent values in equation 1 the value of A is obtained for bare and modified electrode is 0.013 cm^2 and 0.062 cm^2, respectively. These data confirms the enhancement in the electroactive surface area of the PNMCNTPE. This outcome reveals that the modified sensor has good conductive property compare to BCNTPE.

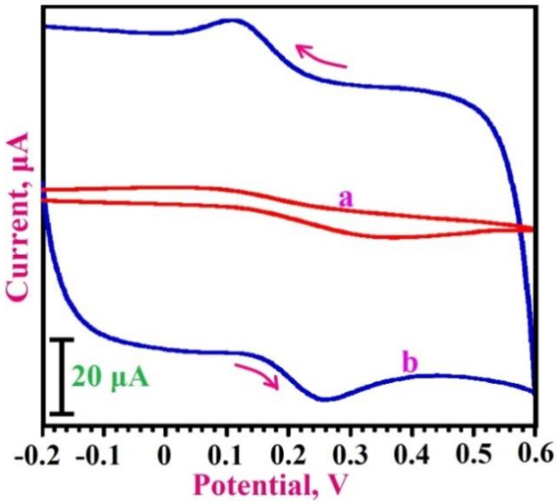


Fig. 3. Cyclic voltammograms of 1 mM $K_4[Fe(CN)_6]$ at BCNTPE and PNMCNTPE

3.2. Optimization of number of scanning segments

To acquire the better catalytic activity of the electrode, optimization of number of sweeping segments in the electropolymerization process plays a significant role in the analysis of VN. With this intension, initially electropolymerization was done through 10 sweeping segments and the CV response was recorded. Next the electrochemical response of VN was obtained at the electrode with 20 sweeping segments and 30 sweeping segments separately. The oxidation peak current correspond to these three studies were demonstrated in Fig. 4. This clearly shows that the sensing effect was maximum at the electrode which was electropolymerized for 20 segments. So, the number of segments for electropolymerization was optimized to 20 segments for further analysis of VN.

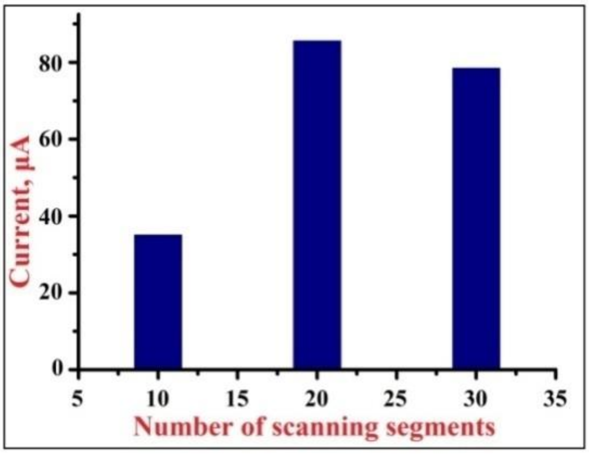


Fig. 4. Plot of number of scanning segments vs. current response

3.3 Study of preconcentration potential and time

Preconcentration potential and time influences the concentration of analyte adsorbed over the electrode surface. This provides the information about the electrochemical response of VN by means of oxidation peak current. To optimize the accumulation potential and time, CV technique was used. Initially preconcentration potential was optimized by changing the initial potential value and keeping the end potential (1.0 V) constant. Initial potential varied from -0.1 to 0.3 V with the increment of 0.1 V in every measurement. From the cyclic voltammograms generated, it was observed that high current effect shown by the electrode towards the electro-oxidation of VN in the potential window from 0.2 to 1.0 V. So this potential window (0.2–1.0 V) is optimized for the remaining analysis of VN. The percentage of current obtained at different potentials were displayed in Fig. 5b.

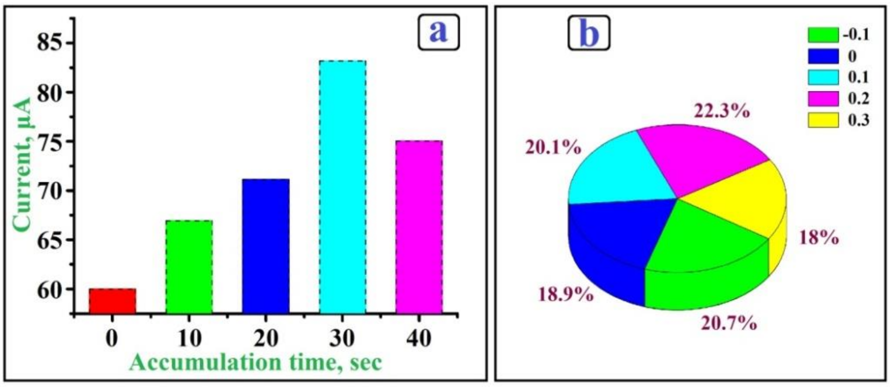


Fig. 5 a) Graph representing current response at different preconcentration time **b)** Chart representing the percentage of current obtained at various preconcentration potentials (accumulation potential varies from -0.1 V to 0.3 V)

Furthermore, in order to optimize the preconcentration time, the investigation was carried out by recording the cyclic voltammograms by varying the time of accumulation from 0–40 seconds. The current response shown by the prepared sensor at different preconcentration time was collected in Fig. 5a. The optimum preconcentration time of 30 seconds was opted for the further investigation of VN. Because, the highest peak current response was acquired at 30 seconds. Further increase in the accumulation time, the current response was declined due to the saturation of VN concentration at the electrode surface.

3.4. Analysis of surface morphology of the electrode

To examine the surface characteristics of the electrode, FE-SEM measurements were carried out. Fig. 6 displays the FE-SEM micrographs of the BCNTPE and PNMCNTPE. From this we can observed the unevenly placed thread like structures of carbon nanotubes were present at the surface of unmodified electrode (Fig. 6A). Whereas at the modified electrode surface (Fig. 6B) the polymer molecules were adsorbed homogeneously and forms the polymeric thin film. This structural transformation contributes the additional surface area. As a result of this the conductivity of the electrode increases and hence it quickens the electron transfer rate.

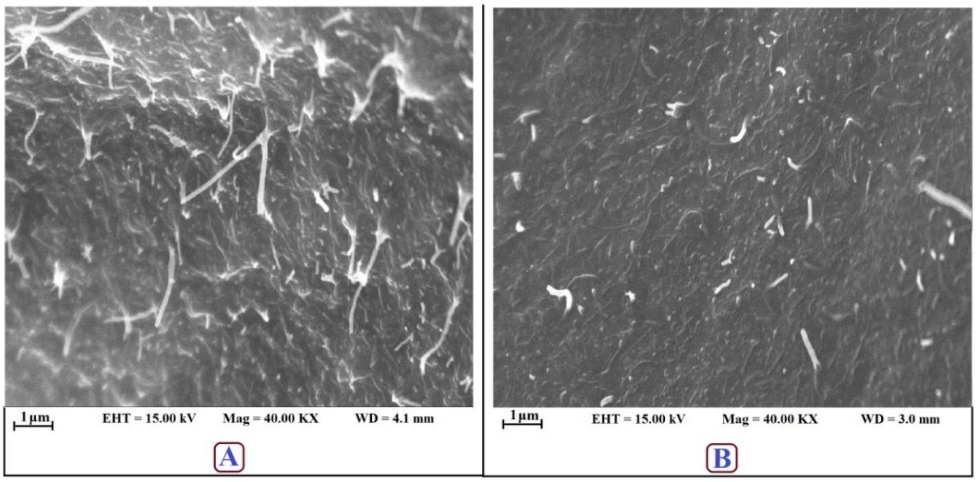


Fig. 6. FE–SEM micrographs of **A)** BCNTPE **B)** PNMCNTPE surface

3.5. Electro catalytic oxidation of VN

With the intension to assess the electrocatalytic behaviour of PNMCNTPE, its CV response was recorded in PBS of pH 7.0 containing 0.1 mM VN at 0.1 V/s. In Fig. 7, curves b and c portrays the cyclic voltammograms generated at PNMCNTPE in the presence and absence of 0.1 mM VN respectively. The obtained outcome displayed that in the forward scanning, VN oxidation takes place with an oxidation peak potential at 0.672 V, whereas in the absence of VN no peak was detected. This confirms the occurrence of peak at 0.672 V is corresponds to the oxidation of VN. Likewise, CV response was also recorded for VN at BCNTPE (Fig. 7, curve a), where a weak response was observed for the oxidation of VN

(I_{pa}= 9.52 µA). Contrary to the BCNTPE, a well-defined anodic peak obtained with 9-fold peak current (I_{pa}= 85.66 µA) at modified electrode confirms the enhanced catalytic activity of PNMCNTPE towards the electro-oxidation of VN. The occurrence of only anodic peak in the forward scanning and the absence of peak in the reverse scanning at bare as well as in modified electrode signifies that the electrochemical reaction of VN is irreversible at both the electrodes.

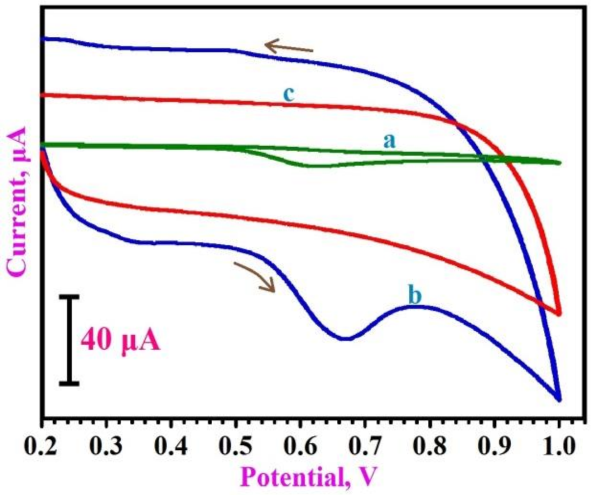


Fig. 7. CV response of 0.1 mM VN at BCNTPE (curve a) and PNMCNTPE (curve b) at pH 7.0. CV curve for PBS of pH 7.0 in the absence of 0.1 mM VN (curve c)

3.6. Influence of solution pH

The influence of solution pH on the electro-oxidation of VN was examined via CV technique in the pH range of 5.5–8.0 at PNMCNTPE. Fig. 8A presents the cyclic voltammograms generated for various pH solutions containing 0.1 mM VN. From this it clearly displays that as the pH of the electrolyte increases from 5.5 to 8.0 the oxidation peak potentials were moved towards the less positive domain. This activity is showed by the electrode due to the protonation and deprotonation property exhibited by VN [35]. Furthermore, the current response of VN at different pH was studied and the acquired current response were collected in Fig. 8C. It was observed that with the increase in solution pH from 5.5 to 7.0 the current sensitivity also increased gradually. Then from pH 7.0 to 8.0 the current sensitivity was declined. We got maximum current response for VN at pH 7.0. So, this pH was opted for the subsequent analysis of VN. The pH reliance of peak current corresponds to the oxidation of VN is possibly due to the adsorption of VN at the modified electrode surface, and also, due to the solubility of VN in different pH solutions.

From the study of anodic peak potential, it exhibits a linear correlation with the solution pH (Fig. 8B) according to the regression equation, Epa (V) = 1.143-0.067 V/pH, R=0.989. From the above equation the slope value is attained as 0.067 V/pH, which obeys the

Nernstian equation (slope value 0.059 V/pH) suggesting the participation of equal number of electrons and protons in the electrochemical process [36,37].

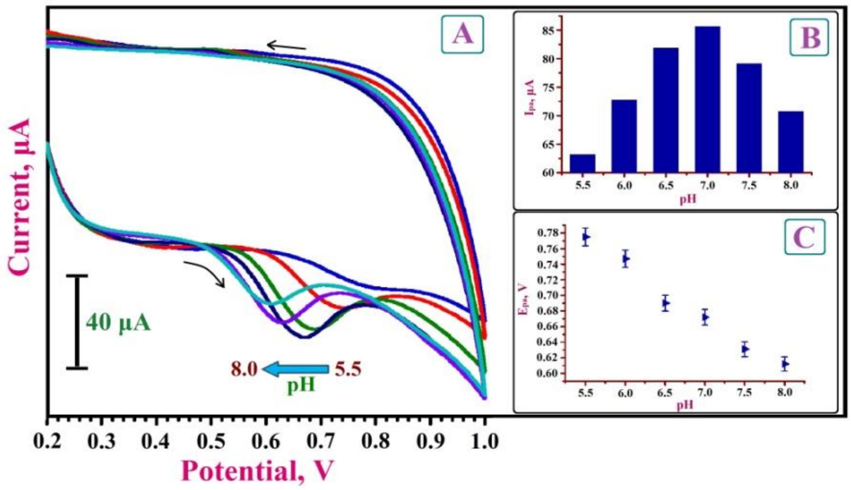


Fig. 8. a) CV curves for 0.1 mM VN at PNMCNTPE in 0.2 M PBS at various pH values from 5.5 to 8.0 **b)** Plot of I_{pa} vs. pH (5.5–8.0). **c)** Graph of E_{pa} against pH

3.7. Effect of potential sweep rate

The cyclic voltammograms obtained for 0.1 mM VN at various sweep rates (0.05 to 0.25 V/s) are displayed in Fig. 9a. It is obvious that by studying the relationship between the sweep rate, and its corresponding peak current and potential, we can gather some information about the electrochemical mechanism takes place at the electrode surface. By utilizing the data collected from the cyclic voltammograms, the linear correlation was observed between the scan rate (ν) and peak current (Fig. 9b) with linearity R= 0.993. This excellent linearity predominantly specifies the adsorption mode of mass transfer process taking place at the electrode. This behaviour was further confirmed by examine the slope of the straight line obtained from the graph of log I_{pa} vs. log ν (Fig. 9c), and it was achieved to be 0.81, which is in close approximation with the theoretically accepted value 1.0 for the adsorption mode of mass transfer phenomena [38,39]. The linear regression equation corresponds to this relationship is log I_{pa} (µA) = 0.810 log ν + 2.629 with R=0.994. Furthermore, it was also observed that with progressive increase in the sweep rate, the peak potential corresponds to the electro-oxidation of VN was also tends to move towards the more positive potential region. For a completely irreversible electrode phenomena, E_{pa} is described using the Laviron's equation as [40]:

$$E_{pa} = K + \frac{RT}{\alpha nF} \ln \nu \tag{2}$$

By utilizing the Laviron's expression, the number of electrons (n) involved over the electro-oxidation of VN was calculated. In the equation 2, E_{pa} denotes the anodic peak potential, F and R have their standard values, T represents the room temperature. From the slope obtained from the linear fit of E_{pa} *vs.* ln ν (Slope=0.072) and by substituting the respective data in the Laviron's equation, the value of n was calculated as 1.64, which is approximately equal to 2.0. The diagrammatic representation of proposed oxidation mechanism of VN is described in Scheme 1 [41].

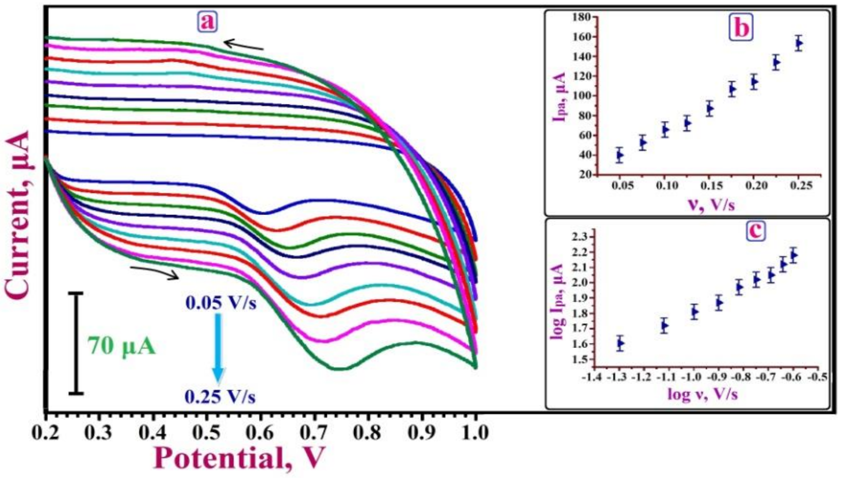
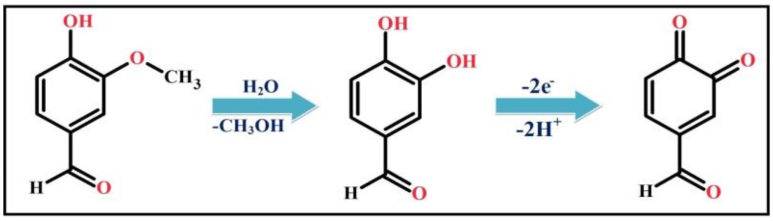


Fig. 9. a) CV curves for 0.1 mM VN at PNMCNTPE in PBS of pH 6.5 at different scan rates, from 0.05-0.25 V/s **b)** Plot of anodic peak current against sweep rate **c)** Graph of log I_{pa} as a function of log ν.



Scheme 1. Oxidation mechanism of VN

The surface coverage (Γ) of VN at PNMCNTPE was computed with the application of the following expression [42]:

$$\Gamma = Q/nFA \tag{3}$$

In the above expression, Q signifies the electric charge attained by integrating the oxidation peak (Coulombs), F symbolize the Faraday constant, A epitomize the geometric surface area of the prepared sensor, n represents the total number of electrons involved in the electro-oxidation of VN. By applying the subsequent values in the equation 3, the value of Γ was evaluated as 2.85 nmol/cm^2.

3.8. Simultaneous detection of VN with CF

The molecules VN and CF are commonly co-exist in most of the confectionary products. If the concentration of these molecules increased it causes acute toxicity to the consumer. Therefore detection of these moieties simultaneously is of great concern. The CV technique was used to detect VN and CF simultaneously at bare and PNMCNTPE in PBS of pH 7.0. Fig. 10 depicts the cyclic voltammograms recorded for 0.1 mM VN and CF at BCNTPE (curve b) and PNMCNTPE (curve a). A well-separated concavity was obtained for VN (0.742 V) in the presence of CF (1.065 V) shows the possibility of simultaneous detection at the modified electrode. Whereas at the unmodified electrode the peaks were overlapped at the potential about 0.900 V, so it is impossible to detect these molecules at BCNTPE.

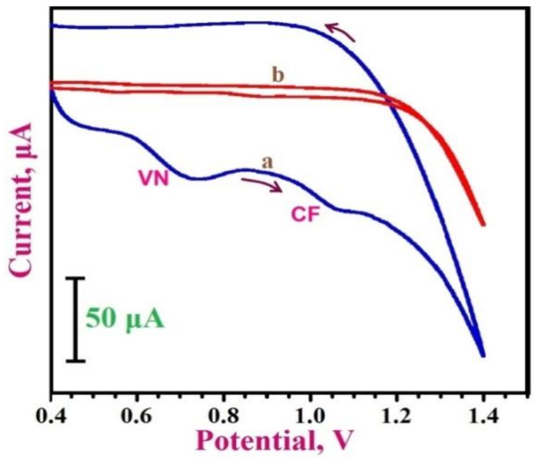


Fig. 10. Cyclic voltammograms generated for simultaneous detection of VN and CF at BCNTPE **(curve b)** and PNMCNTPE **(curve a)**

3.9. Interference study with metal ions

In order to examine the interference effect for the analysis of VN at PNMCNTPE, the cyclic voltammograms were recorded by adding various metal ions to the electrolyte solution containing 0.1 mM VN. The metal ions used for this investigation includes Ba^{2+}, Mg^{2+}, K^{+}, Zn^{2+}, Mn^{2+}, Cu^{2+}, Al^{3+}, Sr^{2+}. The results exposed that with the addition of these metal ions to VN solution, the cyclic voltammetric signals did not effected significantly. It proves that the PNMCNTPE is well suited for the analysis of VN.

3.10. Evaluation of reproducibility, repeatability and stability of the prepared sensor

In order to examine the reproducibility, the proposed electrode was prepared in the similar manner (n=5) and the cyclic voltammograms for 0.1 mM VN was recorded consecutively. From the obtained data, the relative standard deviation (RSD) was calculated and it was obtained as 2.25%. This result proves the excellent reproducibility of the PNMCNTPE.

With the aim to check the repeatability of the PNMCNTPE, the CV responses were recorded at PNMCNTPE for 0.1 mM VN (n=5) sequentially. From the resultant data, the RSD was determined as 1.83%, confirms the admirable repeatable quality of the electrode. With the intension to evaluate the stability of the currently modified sensor, the electrode was scanned continuously for 60 segments in a PBS containing 0.1 mM VN. From the CV outcome it was observed that 94% of its anodic peak height was retained under optimized experimental conditions.

3.11. Real sample analysis and recovery test

With the intension to evaluate the practicality of the developed electrode, the commercially available vanilla flavour was purchased from the local market and was examined via CV technique. The analysis was carried out corresponding to the VN content present in that sample. By the usage of obtained data we calculated the recovery of the sample and were collected in Table 1. The obtained recovery results (99.6–102.8%) suggests that the currently developed electrode can be successfully used for the detection of VN in real food samples.

Table 1. Recovery data of analysed Vanilla flavour sample

Sample	**Added (10^{-5} M)**	**Found (10^{-5} M) (± SD for three replicate measurements)**	**Recovery (%)**
Vanilla flavour	0.8	0.82±0.011	102.80
	1.4	1.39±0.017	99.64
	1.8	1.79±0.022	99.72

3.12. Calibration and evaluation of detection limit

Detection limit (LOD) describes the least possible analyte concentration which can be detected using the any of the technique or instrument. In the present study CV technique was used to evaluate the LOD and LOQ values. The analysis was carried out in PBS of pH 7.0 at PNMCNTPE by increasing the concentration of VN for every successive scan. The concentration of VN was increased from 2×10^{-6} M to 8×10^{-5} M. The data obtained from the recorded cyclic voltammograms, the graph was plotted by taking VN concentration in the x-axis and the peak height value in the y-axis (Fig. 11) and it produced two linear fits. First linear fit was formed in the concentration range from 2×10^{-6} M to 3.5×10^{-5} M and second linear fit was observed from 4×10^{-5} M to 8×10^{-5} M. Slope obtained from the linearity study (concentration range: 4×10^{-5} M to 8×10^{-5} M), and the standard deviation of the 5 successive blank assessments were utilized for the calculation of LOD and LOQ values according to [43–46]:

$$LOD=3S_d/m \text{ and } LOQ=10S_d/m \qquad (4)$$

The value of LOD and LOQ were calculated as 10.1×10^{-7} M and 33×10^{-7} M, respectively.

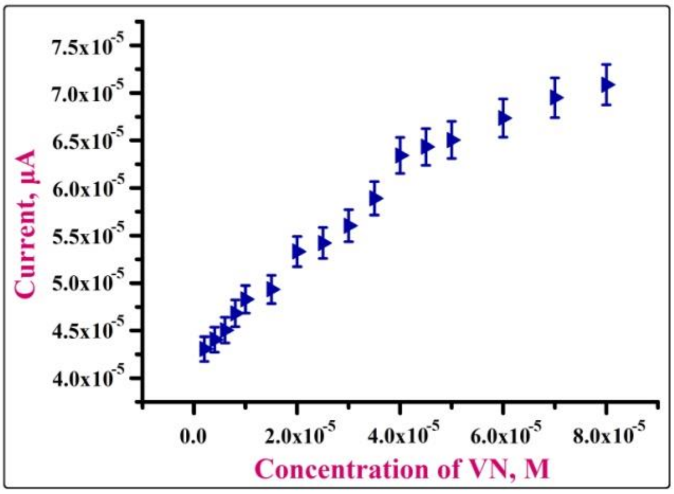


Fig. 11. Graphical representation of anodic peak current at various concentration of VN

Table 2. Comparison of LOD values obtained at different electrochemical techniques

Detection technique	Electrode type	Linear range (M)	LOD (µM)	Reference
SWV	Cylindrical CFME	10×10^{-6}–70×10^{-5}	4.20	[47]
Amperometry	PVC/graphite electrode	66×10^{-5}–920×10^{-5}	290.00	[48]
Sono–SWV	GCE	5×10^{-5}–30×10^{-5}	16.00	[49]
DPV	LCPE	10×10^{-6}–100×10^{-6}	2.88	[50]
CV	PNMCNTPE	4×10^{-5}–8×10^{-5}	1.01	Present work

SWV: Square wave voltammetry; DPV: Differential pulse voltammetry; CFME: Cylindrical carbon fiber microelectrode; PVC: poly(vinyl chloride), GCE: Glassy carbon electrode; LCPE: Lysine modified carbon paste electrode.

As compared with the LOD values obtained for different detection techniques which was collected from previously reported studies, the LOD value obtained in the present work is low. So, the present modified sensor is more sensitive compared to those mentioned in the Table 2.

4. CONCLUSION

In the present study, we successfully prepared the PNMCNTPE based on the electropolymerization technique to explore the electrochemical activity of VN. The developed electrode surface was characterized by the application of FE–SEM micrographs. The PNMCNTPE exhibits improved current sensitivity in comparison with BCNTPE. Moreover, the developed sensor was utilized for the simultaneous detection of VN and CF using CV technique. A lower LOD value (10.16×10-7 M) was estimated for VN. Also, the PNMCNTPE was successfully adopted to detect VN in real sample.

Acknowledgement

We gratefully acknowledge the financial support from the VGST, Bangalore under Research Project. No. KSTePS/VGST-KFIST (L1)2016-2017/GRD-559/2017-18/126/333, 21/11/2017.

Conflict of interest

The authors declare there is no conflict of interest.

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