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An Electrochemical Detection of Vanillin Based on Carbon Black Nanoparticles Modified Screen Printed Carbon Electrode

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From past decades, carbon-based electrochemical sensing electrode materials were developed. Among the all, carbon black (CB) based electrode materials achieved a predominant position in electrochemical sensing application due to its low cost, unique physical and electrochemical properties. Herein, we have fabricated pristine CB as an active electrode material for the detection of VAN (VAN). Initially, the surface and nature of pristine CB material were studied by various characterization methods such as XRD, and HR-TEM analysis. As characterized pristine CB was used for the fabrication of carbon based electrode for electrochemical sensing of VAN. For that, the reported CB/SPCE was subjected to various electrochemical techniques such as cyclic voltammetry and differential pulse voltammetry methods. From the analysis, a low level detection limit (0.039 µM) and high sensitivity of (0.096 $\mu A \mu M^{-1} cm^{-2}$) was achieved for CB/SPCE towards sensing of VAN. Furthermore, the fabricated CB/SPCE electrode shows excellent reproducibility and stability as compared to other carbon based electrode materials. Therefore, we believed that the CB/SPCE sensor is enough electrode for the electrochemical sensing of VAN.

Keywords: Nanocatalyst, Carbon black, Electrochemical sensor, VAN, Cyclic voltammetry

1. INTRODUCTION

Vanillin (4-hydroxy-3-methoxybenzaldehyde, VAN) is one of the phenolic aldehydes and derived from various tropical plants. Mostly, natural vanillin is derived from the vanillin orchid planiforia and beans [1]. Whereas, it is used as a flavoring agent in foods, beverages and pharmaceuticals. Generally, a small quantity of the vanillin product was utilized for the flavoring of food materials due to its high cost. In order overcome such problem, various artificial synthesis and biological manufacturing methods were used for the production of vanillin [2]. In addition to that, it is used for the production of various products such as deodorant, herbicides and house fold products [2]. Moreover, Vanillin exhibits several biological properties such as antioxidant, anti-carcinogenic, anti-mutagenic and anti-microbial activities [3]. Besides, vanillin is used to cure various health problems such as anxiety, digestive problems, stomach pain, and stress [3]. But, large intake of vanillin causes potential health problems such as impaired kidney, spleen and liver functions [2]. Based on the regulation of FDA, concentration level of vanillin in food additives should not exceed of 70 mg kg-1. At the same time, amount of vanillin used for the preparation of various food materials such as chocolate, butter, ice creams are in the range of 25% to 30%. Similarly, the concentration of vanillin in cakes and biscuits are categorized in the range of 0.1% to 0.4%. Aforementioned, the high level utilization of vanillin in Children causes several health problems [2]. Therefore, the optimization of concentration of vanillin is an important aspect for food safety concern and to overcome environmental pollution [3-6]. For that, various methods have been developed for the detection of vanillin such as UV spectrometry [7], GC-MS spectrometry [8], high performance liquid chromatography [9], capillary electrophoresis [10], and electrochemical sensor [11]. Among the all, electrochemical method is considered as more suitable technique due to high sensitivity, selectivity, low cost and simplicity. In case of electrochemical method, high overpotential of vanillin at bare electrode causes fouling effect which leads to the low selectivity and less reproducibility. In order to overcome such problems, different types of carbon materials were used for the modification of electrode surface.

Generally, various carbon materials such as graphene, carbon nanofiber, graphene oxide, carbon nanotube, and carbon black were used for the electrochemical sensing of vanillin due to their high surface area and large conductivity [12-16]. Among the all, the carbon black (CB) is believed as a more active electrode material for the sensing of vanillin. pristine Carbon black is an amorphous quasi structured material with large surface area as compared to other carbon materials. It is composed of sp2 hybridized spherical carbon particles with a diameter of 15-100 nm, which exists in aggregates form with particle size around few micrometer [17-21]. CB exhibits large surface area, high conductivity, abundant pore size, and high defective sites which made them more suitable for electrochemical application [22]. Moreover, it is used as an electrode material for various application such as batteries, fuel cells, oxygen reduction reaction, and electrochemical sensor due to its inexpensive nature [23-26]. Owing to the electrochemical properties, CB shows high electrically conductive properties and it is easily electro catalyze many oxidation/reduction reactions. Further, use of CB as a modifier of electrode will leads to enhance size of analytical signal and electron transfer kinetics. More evidently, Lounasvuori *et al*. fabricated carbon black based electrochemical sensor for the detection of phenolic compounds [27]. Based on the aspects, we have fabricated pristine CB

modified electrode for the electrochemical detection of vanillin. In this work, we have reported the use of carbon black as electrode material for electrochemical sensing of VAN in food samples. For that, the pristine B material was characterized by various techniques such as XRD, and HR-TEM analysis. Further, the electrocatalytic behaviour of bare GCE and that of CB modified SPCE surface was compared. At finally, we have concluded that the CB/SPCE shows high enhanced electrocatalytic activity towards sensing of VAN.

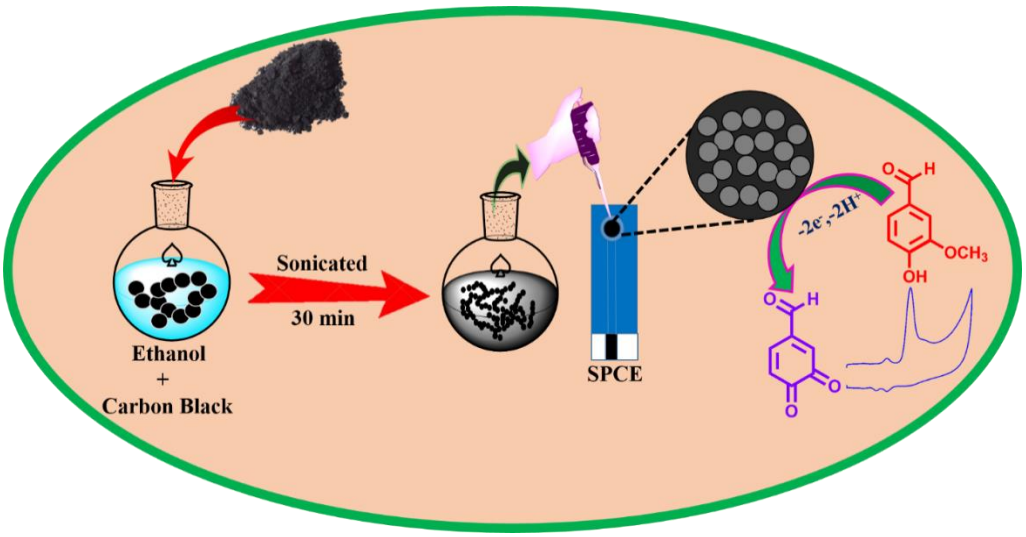
2. EXPERIMENTAL SECTION

2.1. Materials and methods

Vulcan XC-72R Carbon black was purchased from Cabot corporation and research grade o-VAN was purchased from Sigma-Aldrich. Where, phosphate buffer solution (PBS) of pH 7 was used as an electrolyte. It is prepared from 0.05 M Na_2HPO_4 and NaH_2PO_4 salts. 0.05 M H_2SO_4 and 2.0 M NaOH was used to adjust the pH. All these solutions were prepared by using double distilled water. The chemicals were used without further purification.

2.2. Characterization Techniques

The amorphous nature of carbon black was confirmed by Powder X-ray diffraction analysis (XRD, XPERT-3 diffract meter (Cu Kα radiation (K = 1.54 Å)). Whereas, the Surface morphology of pristine Carbon black was studied by HRTEM analysis (TEM, JEOL 2100F). Further, the electrochemical sensing behavior of CB was investigated by cyclic voltammetry (CHI405A) and differential pulse voltammetry (CHI900). For that, typical three electrode system embracing of a platinum wire as auxiliary electrode, SPCE as a working electrode, and Ag/AgCl (standard KCl) as reference electrode was used.



Scheme 1. Schematic representation of CB modified SPCE and its electrochemical applications

2.3. Fabrication of carbon black modified electrode

The pristine carbon black (CB) modified electrode (SPCE) was fabricated by drop casting method. About 5 mg of pristine CB was dispersed in 1mL of ethanol and sonicated for 30 min. After that, about 6 µL of well dispersed CB was drop coated on SPCE and dried in hot air oven. Then the electrode was rinsed with water to remove unbounded particles. Further, the modified electrode was used for all electrochemical studies. The corresponding fabrication of CB/SPCE was shown in (Scheme 1).

3. RESULTS AND DISCUSSION

3.1 Characterization of CB

The amorphous nature of pristine carbon black was clearly estimated by X-ray diffraction technique. XRD pattern of pristine CB was shown in Fig. 1(A). From Fig 1(A), the obtained diffraction peaks of pristine CB were (002), and (100) which is corresponding to the diffraction angle of 24.6°, and 43.3°, respectively. Moreover, the morphology of the pristine CB also confirmed by HR-TEM analysis. TEM images of pristine CB was shown in Fig. 2(A-B). From the images, it is confirmed that the CB particles are spherical in shape. while, the HR-TEM images (Fig. 2(C-D)) also proven that the pristine CB particles was spherical in structure along with a particle size is around 50 nm in range. Besides, the amorphous nuclei of pristine CB that are surrounded by graphitic carbon layers. From the all, it is confirmed that the pristine CB particles are successfully formed by ultrasonication method.

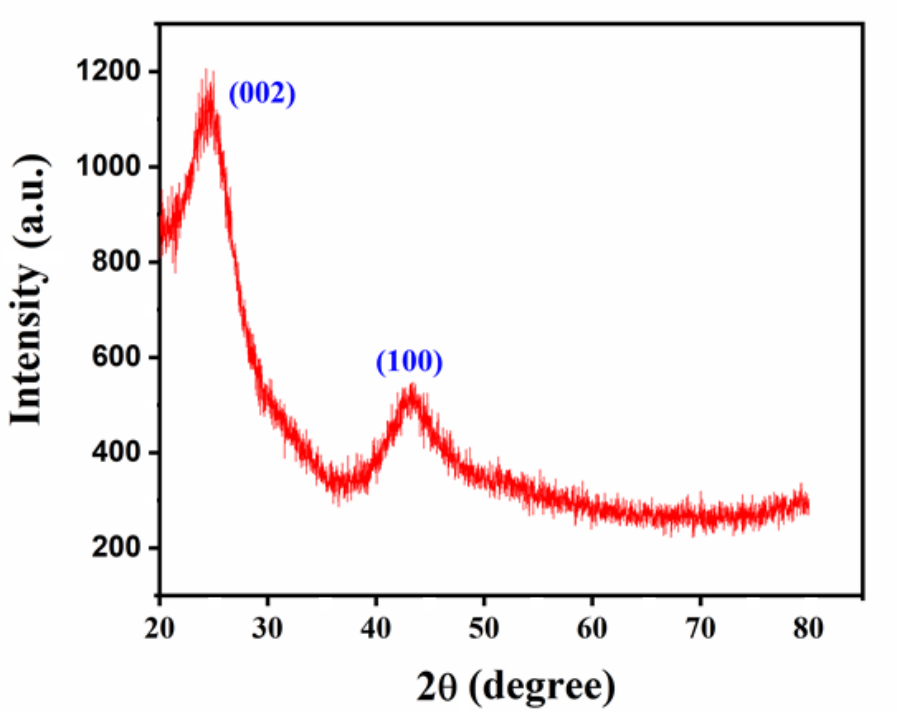


Figure 1. (A) XRD pattern of pristine CB

3.2. Electrochemical behavior of pristine CB/SPCE

The electrochemical oxidation of VAN at pristine CB modified electrode (SPCE) was investigated by using cyclic voltammetry (CV). For that, CV experiment was carried out in presence of 0.05 M PBS (pH 7.0) at a scan rate of 50 mVs^{-1}. The corresponding CV response for bare SPCE and CB/SPCE were shown in Fig. 3(A). From the curve, it is clearly observed that the curve (a,b) represents CV response for bare SPCE and CB/SPCE without the addition of VAN. While, the CV response for bare SPCE and CB/SPCE in presence of VAN were indicated in curve (c,d). There is a small current response was observed for the addition of 200 µL VAN at bare SPCE. As compared to bare SPCE, a sharp well defined oxidation peaks were observed at a potential of 0.485 V, and 0.308 V for the oxidation of VAN. In addition to that, two reduction peaks were observed at a potential of 0.308V and 0.227 V in the first segment. The appearance of well-defined redox peaks at CB/SPCE is mainly arises from the existence of large number of defective sites on the CB. Moreover, the presence of large surface area also plays an important role in enhanced electrocatalytic activity of pristine CB modified electrode.

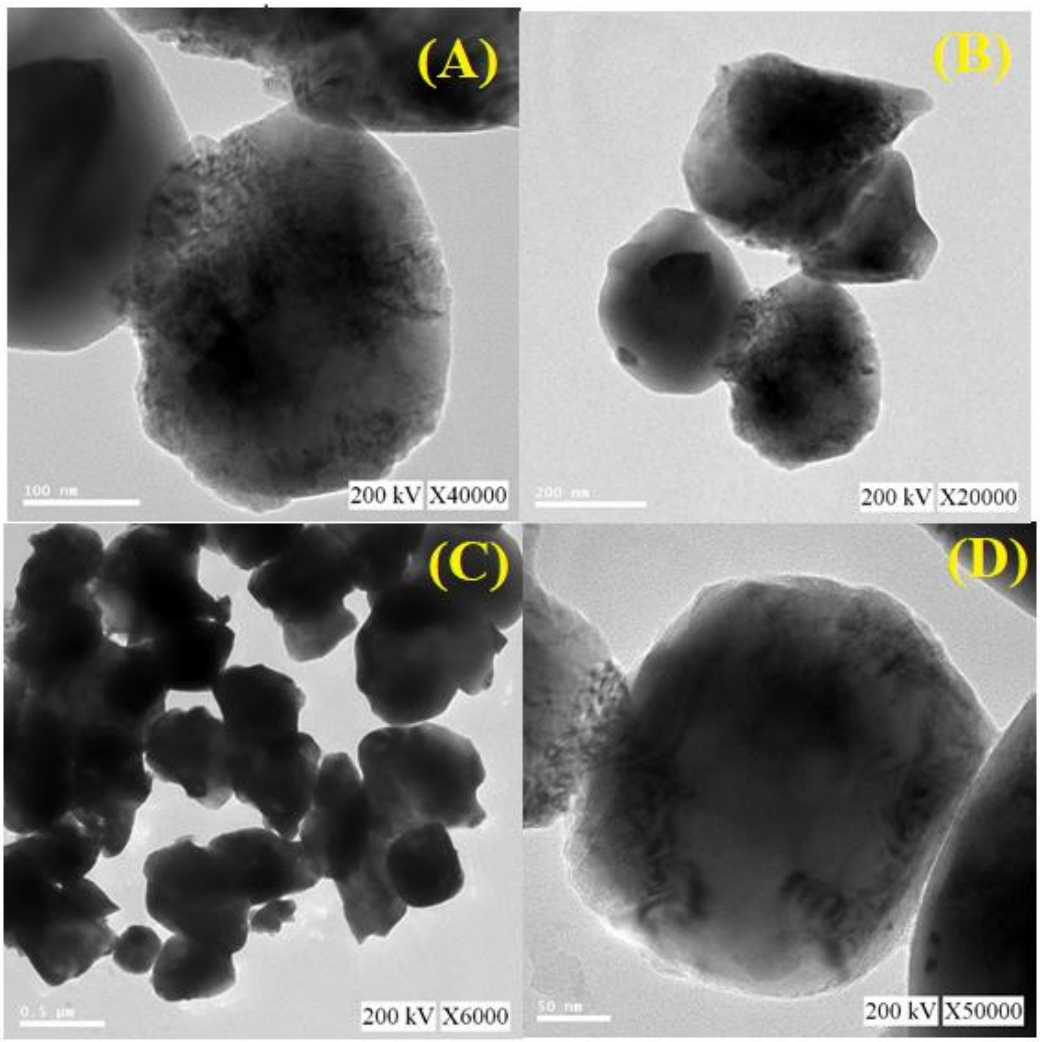


Figure 2. (A, B) TEM images of pristine CB. (C-D) HR-TEM image of pristine CB

3.3. Effect of concentration for electrochemical detection of VAN at CB/SPCE

Further, the electrochemical activity of CB/SPCE was investigated by varying the concentration of VAN. While CV experiment was performed in presence of N_2 saturated PBS (pH 7.0) at a scan rate 50 mVs^{-1}. The concentration of VAN is varied from 50 to 450 µM. Fig. 4(A), indicates the corresponding CV curve for variation of VAN concentration at CB/SPCE. From the Fig. 4(A), it is clearly observed that the redox peak current increase with increase in concentration of VAN. Whereas, there is no significant peak shift was observed during variation in concentration of VAN. Further, the increment in current vs. concentration was indicated in bar diagram of Fig. 4(A), (inset)). Similarly, the linear curve for logarithm of oxidation peak current vs. logarithm of VAN concentration is shown in Fig. 4(B). From the curve, linear regression equation was calculated as $y = 0.201x - 0.1046$ ($y = I_{pa}$ (µA), x = VAN (µM)), and correlation coefficient $R^2 = 0.9953$. The obtained slope value resembles that the overall electrochemical mechanism of VAN at CB modified electrode follows first order kinetic mechanism.

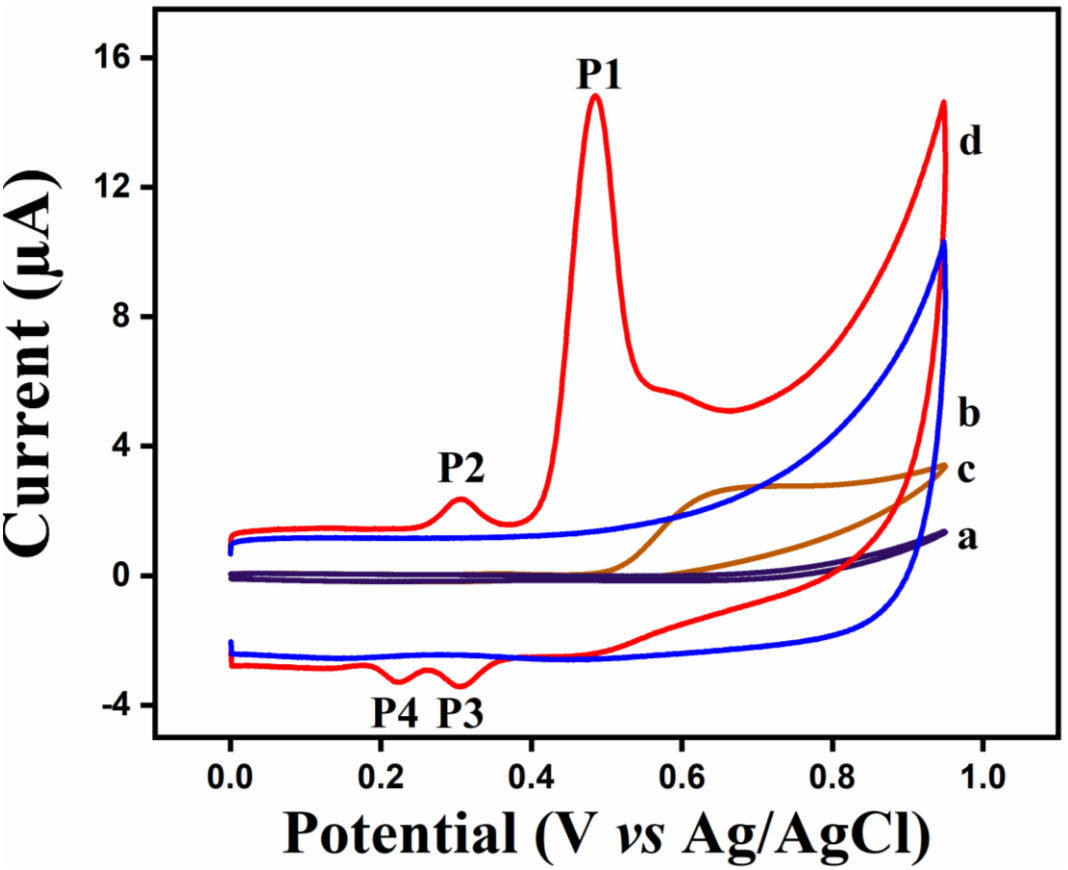


Figure 3. (A) CV response for (a) SPCE (b) r CB/SPCE modified electrode (without VAN) (c) CV response for addition of VAN at bare SPCE (d) CV response for addition of VAN at CB/SPCE

3.4. Effect of scan rate for electrochemical detection of VAN at CB/SPCE

The electrochemical sensing mechanism of VAN at CB modified electrode (CB/SPCE) was influenced by various parameters such as scan rate, and pH of the electrolyte. Whereas, the influence

of scan rate on sensing of VAN at CB/SPCE was studied by using cyclic voltammetry. CV analysis was carried out in N_2 saturated PBS (pH 7.0) with addition of (200 µM) VAN. In addition to that, scan rate was varied from 10 to 240 mVs^{-1} and resultant current response is indicated in Fig. 5(A). From the Fig. 5(A), it is clearly estimated that the redox peak current increase with increase in scan rate during electrochemical reaction. The relationship between redox current vs. scan rate is shown in Fig. 5(B). The corresponding linear equation was deduced from the linear curve along with a correlation coefficient of y = -0.0768x -1.809 (y = (I_{pa} (µA)), x = (ν (mVs^{-1})), R^2= 0.9933. Similarly, the linear relationship between peak potential vs. log scan rate is shown in Fig. 5(C). From the curve, the linear regression equation was deduced as y = 14.156x – 5.5976 (y = (E_{pa} (v)), x = log (ν (mV s^{-1})) and correlation coefficient of R^2 = 0.9979. From the linear plot, it is concluded that the overall electrochemical reaction of VAN is adsorption-controlled process. Similarly, the reaction mechanism exhibits low kinematic limitation for the detection of VAN. Therefore, we believed that the pristine CB modified electrode is highly active electrode material for electrochemical sensing of VAN.

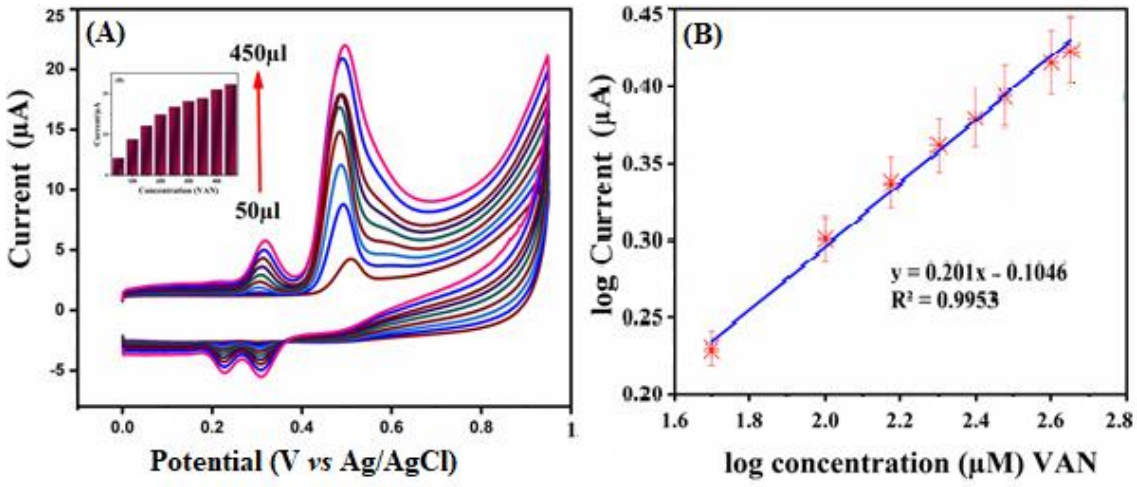


Figure 4. (A) CV response for concentration variation of VAN (50 – 450 µL) at CB/SPCE. (A (inset)) Corresponding bar diagram (Current vs. Concentration). (B) calibration plot Log current vs log concentration of VAN.

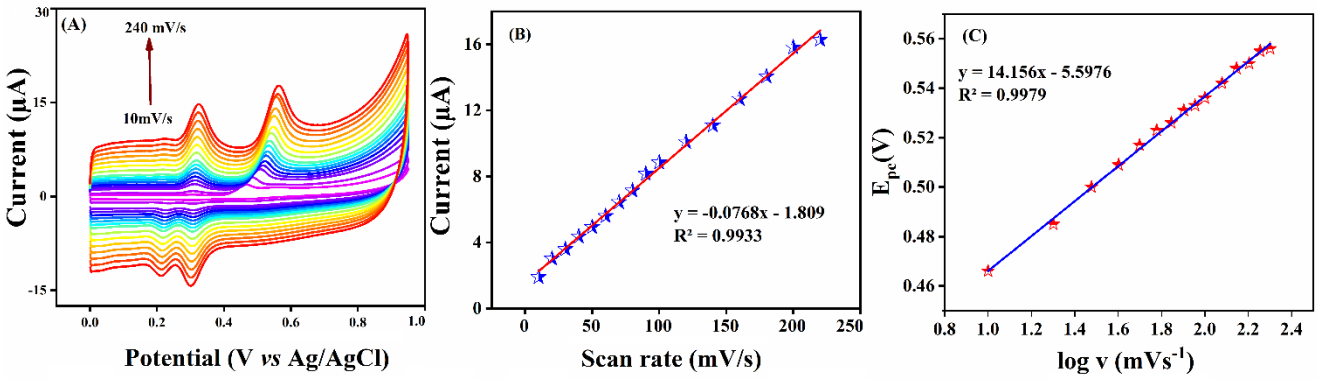


Figure 5. (A) CV response of CB/SPCE varying scan rate (10-240 mVs^{-1}) with presence of VAN 200µM (B) Linear calibration plot for current vs. scan rate (C) Corresponding linear plot for potential vs. logarithm of scan rate

3.5. Effect of pH for electrochemical detection of VAN at CB/SPCE

The influence of pH on the electrochemical mechanism of VAN at CB/SPCE was studied by CV analysis. The CV experiment was performed in presence of N_2 saturated PBS with varying pH from 3 to 9. The obtained CV results is shown in Fig. 6(A). From the result, it is evidently proven that the peak current decreases with increase in pH from 3 and 5 due to the involvement of protons. More precisely, the peak potential also shifted towards higher potential value. Similarly, the peak current was decreases for pH 9. While, the higher redox current with lower potential was obtained for pH 7. Therefore, the corresponding response for current vs. pH is demonstrated in linear plot Fig. 6(B). From the all, we have concluded that the pH 7 is more suitable for electrochemical detection of VAN.

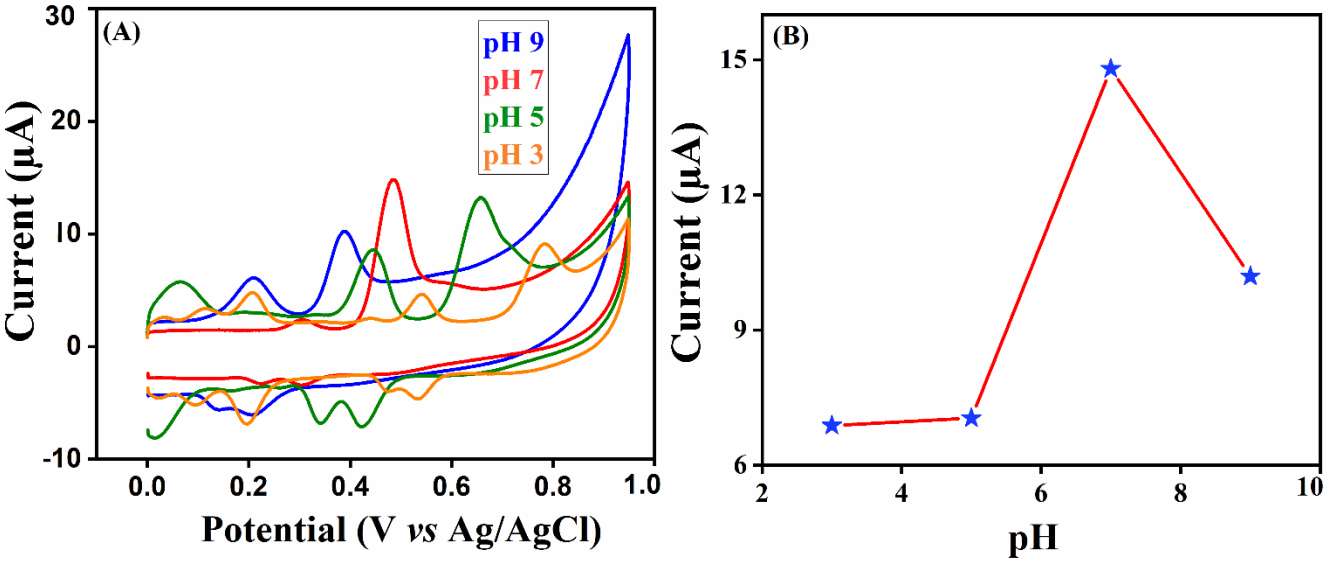


Figure 6. (A) CV response of CB/SPCE different pH (3-9) at scan rate of 50 mVs^{-1}. (B) variation of current vs. pH.

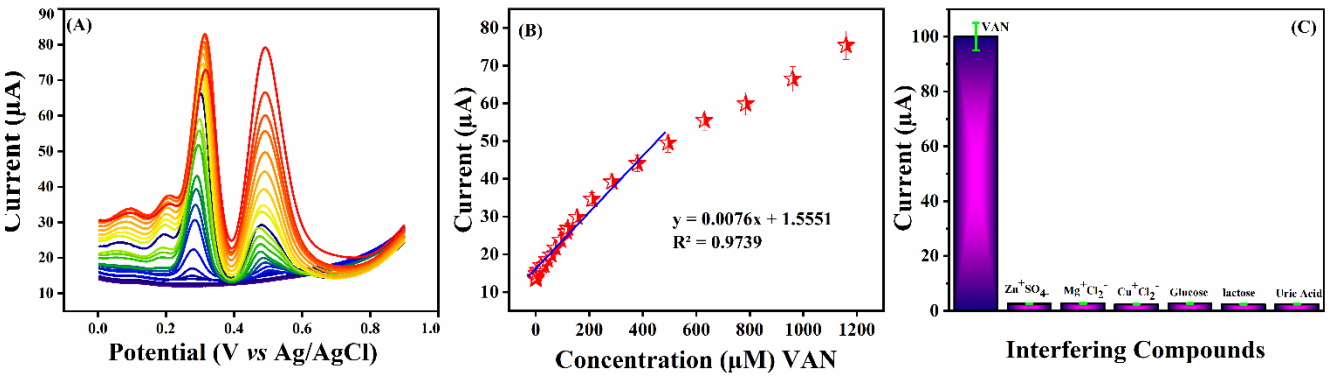


Figure 7. (A) DPV response of CB/SPCE for addition of VAN (0.1- 495µM) (B) The calibration plot of peak current vs. Concentration of VAN. (C) Error bar diagram for interfering species in DPV.

3.6. Differential pulse voltammetry for detection of VAN at CB/SPCE

Generally, the detection of low concentration of any analyte molecule was studied by differential pulse voltammetry technique. DPV experiment was performed in presence of N_2 saturated PBS (pH 7.0) at a scan rate of 50 mVs^{-1}. For the experiment, concentration of VAN is varied from 0.1 to 1160 µM. The corresponding DPV curves were demonstrated in Fig. 7(A). From the curve, it is clear that the redox current increases with increase in concentration of VAN. The resultant linear variations are indicated in linear plot (0.1 – 495 µM) between redox current vs. concentration of VAN and as shown in Fig. 7(B). From linear plot, the linear regression equation is written as y = 0.0076x +1.555 (y = I_{pa} (µA), x = VAN (µM)), and a correlation coefficient obtained as R^2 = 0.973. Moreover, the limit of detection and sensitivity of the proposed CB/SPCE towards sensing of VAN, was deduced from the slope of linear curve. Therefore, the obtained slope value is substituted in equation (1),

$$LOD = 3\sigma/s \quad (1)$$

Whereas, the σ standard deviation of the blank values, S is slope of linear curve. After substitution in equation (1), the LOD and sensitivity of proposed sensor were calculated as 0.039 µM. The obtained values are compared with previous reported VAN sensors (Table 1). From the all, it is concluded that the proposed sensor CB/SPCE is more acceptable for the sensing of VAN.

Table 1. Comparison studies for the VAN at various modified electrode

Modified Electrode	**Linear range (µM)**	**Detection limit (µM)**	**Technique**	**Ref.**
Ar-Gr/GCE	2-70	1	DPV	[28]
TBAC-900/GCE	5-1150	0.68	LSV	[29]
GCE	50-300	0.16	SWV	[30]
Gr/GCE	0.6-48	0.05	DPV	[31]
CoS nanorods/GCE	0.5-56	0.07	DPV	[32]
Disposable SPCE	5-400	0.4	SWV	[33]
PVC-graphite composite	660-920	290	Amperometric	[34]
Ag NPs/GN/GCE	2-100	0.332	SWV	[35]
Cylindrical CFME	10-700	4.2	SWV	[36]
CB/GCE	0.1-495	0.039	DPV	This work

3.7. Selectivity, stability reproducibility studies at CB/SPCE

Generally, the investigation of selectivity of proposed sensor was estimated by anti-interference studies. Not only the interference studies, stability and reproducibility also play a vital role in practical application of any electrochemical sensor. Therefore, the selectivity of CB/SPCE towards sensing of VAN was performed in presence of N_2 saturated PBS (pH 7.0) at a scan rate of 50mVs^{-1}. Besides,

various organic compounds and metals ions were used for the investigation of selectivity. In this case, organic molecules namely vanillic acid, 4-hydroxybenzaldehyde, glucose, fructose, and some metal ions like Cu^+, K^+, Na^+, and Mg^+ were used. For experiment, 100-fold excess concentration of interferent species were added in presence of VAN molecules. Moreover, the corresponding bar diagram in Fig. 7(C) indicates percentage of influence on the redox current. From the diagram, it is clear that the interferent species does not show significant influence on the redox current of VAN. More precisely, the influence of interferent species were negligible and less than 5%. From the result, it is concluded that the proposed CB/SPCE sensor shows excellent selectivity towards sensing of VAN. Further, the reproducibility test for CB/SPCE was investigated in presence of four different electrodes with an operational condition of N_2 saturated PBS (pH 7.0) at a scan rate of 50 mVs^{-1}. The obtained CV results proved existence of excellent reproducibility of CB/SPCE. Similarly, the stability test for CB/SPCE towards sensing of VAN was estimated in same working condition. Cyclic stability test of CB/SPCE was performed up to 100 cycles. From the results, it is found that the CB modified electrode exhibits an excellent stability towards sensing of VAN. All the results proved that the proposed CB/SPCE sensor is more suitable for the electrochemical sensing of VAN.

4. REAL SAMPLE ANALYSIS

To check the practical feasibility of CB modified electrode, the suggested sensor subjected for real sample analysis. The chocolate was purchased from local shop in Taipei. The sample was prepared by grounding the chocolate in mortar to fine powder. About 2 g of powder sample was dispersed in (5%) ethanol followed by addition of pH 7 (95%) and the solution was sonicated for 30 minutes and supernatant solution filtered. The filtered solution was further used as real sample. Different amount of prepared sample was added in PBS solution to determine the recovery amount of VAN shown in Table 2. From the table 2, it is confirmed that the CB modified electrode has good practical feasibility for the determination of VAN in chocolate. Therefore, the proposed sensor was appropriate for determination of VAN [37].

Table 2. Detection of VAN in real sample at CB/SPCE (n = 3)

Sample	Added (µM)	Found (µM)	Recovery (%)	RSD (%)
Chocolate	0	Not found	Not found	Not found
	50	50.5	101.0	1.3
	80	81.9	102.3	1.6
	110	111.8	101.6	1.2

5. CONCLUSION

Herein, we have developed a Simple and innovative approach for the development of pristine carbon black (CB) based electrochemical sensor. For that, the pristine CB was characterized by various analytical technique namely XRD, and HR-TEM analysis. After that, fabricated pristine CB based electrode material (CB/SPCE) was utilized for the electrochemical sensing of VAN (VAN). From the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments, low detection limit 0.039 μM and high sensitivity of 0.096 $\mu A \mu M^{-1} cm^{-1}$ were estimated for the detection of VAN. Similarly, the fabricated CB/SPCE exhibited an excellent anti-interferent activity, reproducibility and stability towards sensing of VAN. All the results proved that the fabricated pristine CB based electrode material is highly acceptable for electrochemical sensing of VAN.

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