



# Electrochemical Preparation of Poly(arginine)-Modified Carbon Nanotube Paste Electrode and its Application for the Determination of Pyridoxine in the Presence of Riboflavin: An Electroanalytical Approach

Girish Tigari<sup>1</sup> · J. G. Manjunatha<sup>1</sup>

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## Abstract

A simple poly(arginine) film-modified carbon nanotube paste electrode (PAMCNTPE) was prepared using cyclic voltammetry (CV). The devised sensor was subjected to field-emission scanning electron microscope (FESEM) and CV characterization. The sensing of 0.1 mM pyridoxine (PY) was upgraded at PAMCNTPE as compared to the bare carbon nanotube paste electrode (BCNTPE). The PAMCNTPE detects the 0.1 mM PY at a specific potential 0.727 V with a current response of 10.68  $\mu\text{A}$ . In the case of BCNTPE, the PY appeared at 0.798 V with a current 2.90  $\mu\text{A}$ . The proposed analytical method was optimized by prime parameters such as the impact scan rate, pH and PY concentration. Under optimal conditions, the concentration of PY is directly proportional to oxidation current ( $I_{pa}$ ) in linear range 2–10  $\mu\text{M}$ , and 10–80  $\mu\text{M}$  with a detection limit (LOD) of  $9.6 \times 10^{-7}$  M and limit of quantification (LOQ) of  $3.21 \times 10^{-6}$  M. The simultaneous determination, concentration variation analysis of PY is performed with riboflavin (RF) and interference analysis in detecting PY also examined. The proposed sensor was effectively applied for the determination of PY in natural food supplement with excellent recovery.

**Keywords** Poly(arginine) · Carbon nanotube · Pyridoxine · Riboflavin · Cyclic voltammetry

## 1 Introduction

PY (vitamin B<sub>6</sub>) is an aqueous soluble B-vitamin, and it is involved in human metabolism and biochemical reactions. PY is required for the human body to maintain physical and psychological health. It is having a significant role in the synthesis of noradrenaline, dopamine, serotonin, and histamine in the human body. It is involved in the production of red blood cells (RBC) and reduces the risk of colorectal cancer. It acts as a coenzyme for many enzymatic reactions. Its inadequacy causes neurological and skin disorders [1–5]. RF (vitamin B<sub>2</sub>) belongs to B-group of vitamins which are found in an egg, meat, liver, and milk as a micronutrient. It is essential for the human body. Lack of RF in the human body causes skin and eye problems. These B-vitamins play a substantial role in human biochemistry; thus, it is

necessary to develop a simple and quick analytical method for the determination of PY and RF [6–8]. There were previously reported a variety of analytical techniques such as chromatography, spectrophotometry, fluorescence spectroscopy [9–11], etc. However, these methods are costly and time-consuming analytical methods. The best substitute for the above methods are electroanalytical approaches like mesoporous TiO<sub>2</sub> and SnO<sub>2</sub> nanocatalyst-modified glassy carbon electrode, cobalt hexacyanoferrate-modified carbon paste electrode, carbon paste electrode modified with crown ethers, multi-wall carbon nanotube-modified carbon-ceramic electrode, copper nanoparticle-modified polycrystalline gold electrode, platinum electrode, electro-deposition of gold nanostructure-modified carbon paste electrode, etc. [12–18].

In sensor fabrication, the carbon nanotubes (CNTs) were frequently used due to their characteristic properties such as high electrical conduction, extreme stability, low noise, long voltage domains, and easy renewability [19, 20]. The polymeric films such as poly(glycine), poly(nigrosine), poly(methyl Orange), poly(rosaniline), solid R, etc. were used for the voltammetric analysis of biomolecules, because

✉ J. G. Manjunatha  
manju1853@gmail.com

<sup>1</sup> Department of Chemistry, FMKMC College, Mangalore  
University Constituent College, Madikeri, Karnataka, India

the polymerization films on the surface of electrode provide conducting path, swift electron transfer, and larger effective surface area. The surface modification by a polymer is a simple and effective approach in dealing with electroanalysis of bioactive molecules [21–24]. To the best of our knowledge, there is no electrochemical sensor based on poly(arginine)-modified carbon nanotube paste electrode for the voltammetry of pyridoxine in the presence of RF.

## 2 Experimental Part

### 2.1 Chemicals and Preparations

Pyridoxine, Riboflavin, and Arginine procured from Molychem, India. Carbon nanotubes are purchased from Sisco laboratories Maharashtra. Silicone oil is brought from Nice Chemicals India. All other chemicals are of A.R grade. The 0.1 M phosphate buffer solution (PBS) of various pH is prepared by intermixing of suitable amount  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$ . The 0.1 mM RF, PY, and 1 mM arginine solutions were freshly prepared using double distilled water.

### 2.2 Apparatus Used

All CV measurements were performed through CHI-6038E (Electrochemical Analyser, USA) in connection with a standard three-electrode arrangement and a computer for information storage and handling. The BCNTPE and PAMCNTPE were used as a working electrode, and a saturated calomel electrode (SCE) and a platinum wire were utilized as reference electrode and auxiliary electrode, respectively. All current measurements are taken with background current. All electrochemical experiments were done at lab temperature.

### 2.3 Development of Carbon Nanotube Paste Electrode

The carbon nanotube paste electrode (CNTPE) is fabricated by hand mixing of carbon nanotubes and silicone oil (60:40%, w/w) in an agate mortar to attain uniform paste, and the obtained paste is packed into the tip of Teflon tube and leveled out by tissue paper.

## 3 Results and Discussion

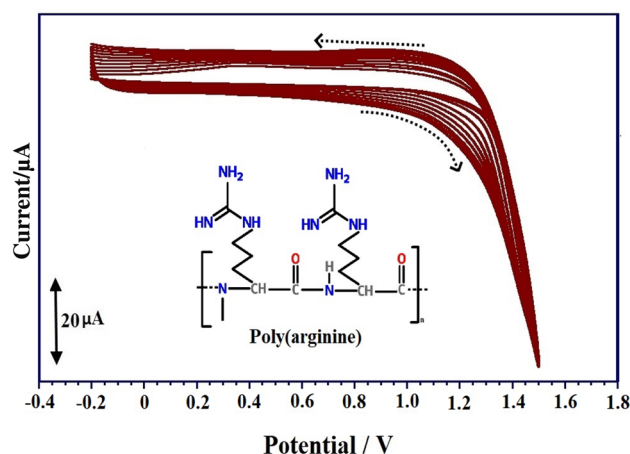
### 3.1 Electrochemical Deposition of Poly(arginine) on Electrode Surface

Amino acid functionalization and polymerization were extensively used for surface modification of electrode due to their high biocompatibility, mechanical strength, easy

modification, little cost, and outstanding film-forming capability. The  $-\text{NH}_2$  and  $-\text{COOH}$  groups of amino acids play a key role in the electro-polymerization process. The polymer modified electrode surface shows excellent electrocatalytic properties in sensing the bioactive molecules. CV is a suitable approach to develop a polymer layer on an electrode surface. The electro-deposition poly(arginine) was performed in potential domain  $-0.2$  to  $1.5$  V with the presence of 1 mM arginine solution in 0.1 M PBS of pH 5.5, at potential sweep rate 0.1 V/s for 10 consecutive cycles as depicted in Fig. 1. It can be seen in figure that the cyclic voltammetric curves were gradually sloped downwards as cyclic period rises. This shows the formation of poly(arginine) thin layer on the surface of the carbon nanotube paste electrode. The poly(arginine)-coated carbon nanotube paste electrode is cleaned with little water to arise the unreacted arginine and used as a sensor for PY detection. The ten multiple cycles are optimized for electrochemical analysis PY.

### 3.2 Electroanalytical Characterization of BCNTPE and PAMCNTPE

The voltammetric behavior of BCNTPE and PAMCNTPE for standard 0.1 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]$  was performed by CV in 0.1 M KCl at 0.1 V/s sweep rate as displayed in Fig. 2. The BCNTPE (curve a) characterizes the  $\text{K}_4[\text{Fe}(\text{CN})_6]$  oxidation at 0.327 V with a current 5.25  $\mu\text{A}$  and reduction at 0.164 V with 3.22  $\mu\text{A}$  current response. PAMCNTPE improves the electrochemical profile of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  by detecting anodic potential at 0.283 V with 10.85  $\mu\text{A}$  current response and anodic potential at 0.187 V with 8  $\mu\text{A}$  current response, so the constructed arginine polymer layer on carbon nanotube paste electrode improves the current–voltage characteristics of  $\text{K}_4\text{Fe}(\text{CN})_6$  with quasi-reversible behavior.



**Fig. 1** Electrochemical polymerization of L-arginine (1 mM) on BCNTPE in PBS, pH 5.5 for ten multiple scans

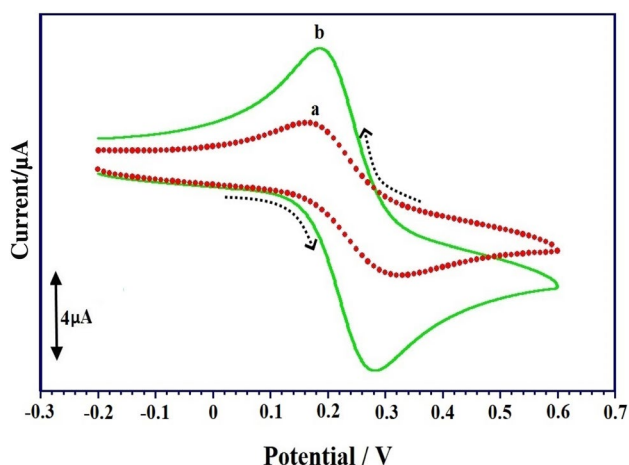


Fig. 2 Electrocatalytic performance of BCNTPE and PAMCNTPE

### 3.3 FESEM Characteristics of BCNTPE (curve a) and PAMCNTPE (curve b) Surfaces

The electroanalytical sensing is a surface-based phenomenon; hence, the surface topography of electrode is important in electroanalysis. This influences the sensing capacity of the electrode, effective surface area, electrode kinetics, etc. Therefore, it is so essential to know the surface morphology of the electrode. The surface characterization was performed using FESEM for BCNTPE and PAMCNTPE, as illustrated in Fig. 3a, b, respectively. The BCNTPE morphology was irregular arrangement whereas in case MCNTPE symmetric surface was observed, which confirms the modification BCNTPE with poly(arginine).

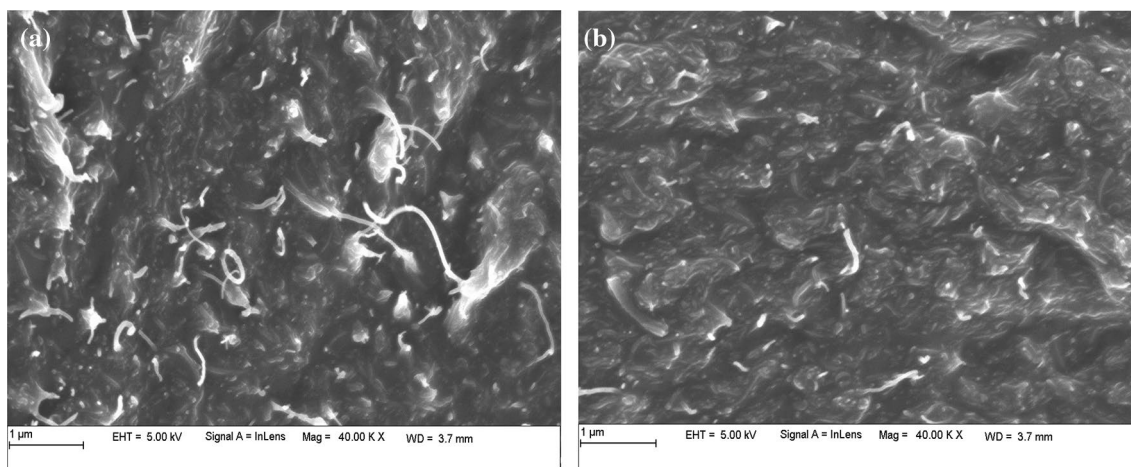


Fig. 3 FESEM surface-magnified images of BCNTPE (a), PAMCNTPE (b)

### 3.4 Electrocatalytic Effect in Sensing PY

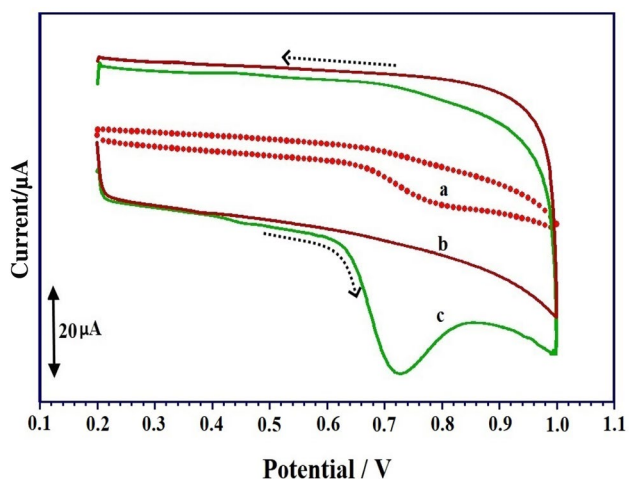
The electrooxidation of 0.1 mM PY was analyzed by CV in the potential range 0.2–1.0 V at sweep rate 0.1 V/s in 0.1 M PBS of pH 6.5, as illustrated in Fig. 4. At BCNTPE PY was detected at potential 0.798 V with a small current response (2.9  $\mu\text{A}$ ), but at PAMCNTPE, the overpotential is reduced, and the current response was enriched due to the catalytic effect of poly(arginine) in sensing PY. The fine-tuned sensing of PY at PAMCNTPE appeared at specific potential 0.727 V with current response 10.71  $\mu\text{A}$  with irreversible behavior. In absence of PY (curve b) the characterized CV portrays no peak at PAMCNTPE.

### 3.5 Potential Sweep Rate Effect

The potential scan rate study is a key parameter in electroanalysis; it is carried out to analyze the electrode kinetics. The impact of sweep rate from 0.1 to 0.250 V/s on the electrocatalytic oxidation of PY is analyzed by CV in 0.1 M PBS pH 6.5, as shown in Fig. 5a. The scan rate affects the current sensitivity of 0.1 mM PY linearly. The plot  $v^{1/2}$  vs.  $I_{pa}$  (Fig. 5b) shows the linear dependence of the oxidation peak current of PY by validating linear equation  $I_{pa}$  (A) =  $1.08 \times 10^{-5} + 6.485 \times 10^{-5} v^{1/2}$  (V/s) with a coefficient of correlation of 0.99. This elucidates that the electrode process is under diffusion controlled. The number of electrons transferred in PY oxidation can be calculated using the standard equation [25]:

$$E_{pa} = E_o - (2.3 RT/anF) \cdot \ln v,$$

where  $n$  is the number of electrons transferred,  $R=8.314$  J.K/mol (real gas constant),  $T$  is the temperature,  $F$  is the Faraday's constant (96,485 C/mol), and  $\alpha$  (charge transfer

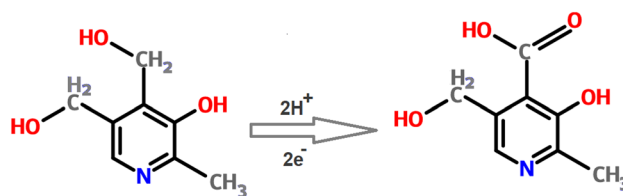


**Fig. 4** Cyclic voltammograms of electroanalysis of PY (0.1 mM) at BCNTPE (curve a), PAMCNTPE (curve c), and cyclic voltammogram of blank (curve b) at PAMCNTPE in PBS, pH 6.5, with sweep rate 0.1 V/s

coefficient) is assumed to be 0.5 in a completely irreversible electrode phenomena [26] and electron transfer evaluated as  $1.72 \sim 2$ . Electron transfer mechanism of PY is predicted as shown in Scheme 1. The effective surface area of PAMCNTPE can be determined using a standard formula [27]:

$$I_{pa} = 2.69 \times 10^5 n (an)^{1/2} AD^{1/2} C v^{1/2},$$

where  $I_p$  is the peak current (A),  $n$  is the number of electrons,  $A$  is the electroactive area ( $\text{cm}^2$ ),  $D$  is the coefficient of diffusion ( $\text{cm}^2/\text{s}$ ),  $C$  is the concentration of the electroactive analyte ( $\text{mol}/\text{cm}^3$ ), and  $v^{1/2}$  is the square root of sweep rate (V/s). The diffusion coefficient value was obtained from

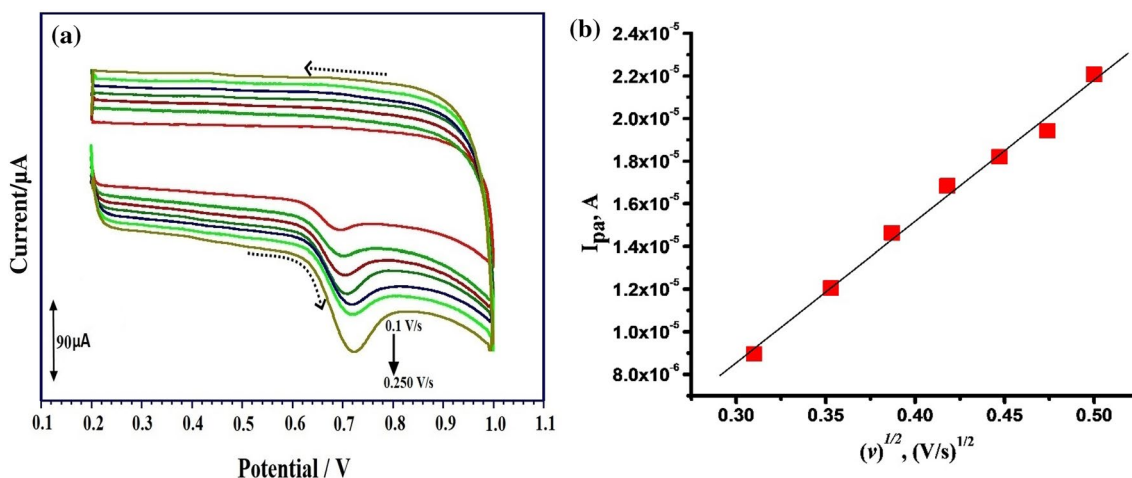


**Scheme 1** Oxidation mechanism of PY

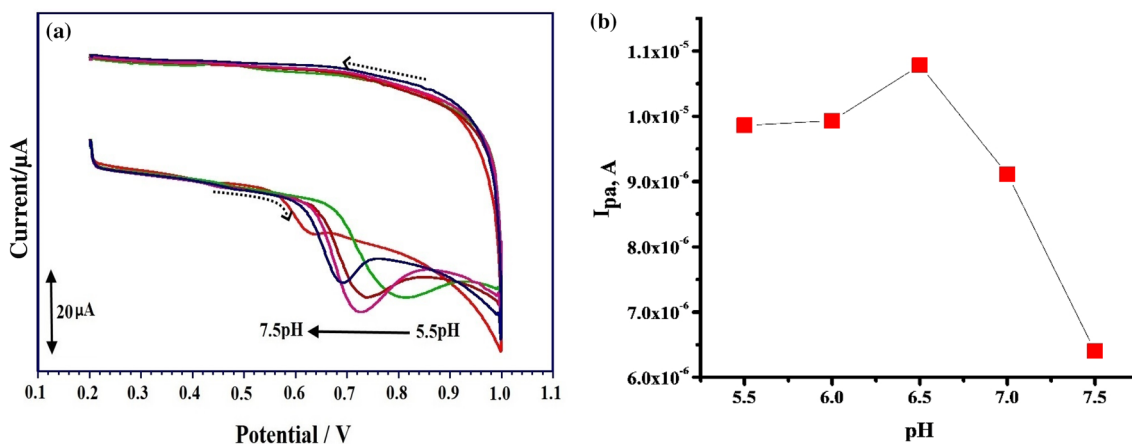
the slope of  $I_{pa}$  vs.  $v^{1/2}$  plot. The active surface area of the PAMCNTPE electrode is calculated using the Randles equation and found to be  $0.082 \text{ cm}^2$ .

### 3.6 Impact of pH of Supporting Electrolyte

The pH of supporting electrolyte has marked effects on the electroanalysis of bioactive molecules, and the pH optimization can improve the analytical performance of the electrode. Therefore, the influence of pH from 5.5 to 7.5 for the electroanalytical determination of PY was studied by using CV at sweep rate 0.1 V/s as displayed in Fig. 6a. As the pH rises, peak potential of PY is lifted towards the negative direction. The graphical plot of pH vs.  $I_{pa}$  (Fig. 6b) gives the high current signal at pH 6.5 at which rapid electron transfer takes place; for further increase or decrease in the pH, the peak current decreases. Therefore, pH 6.5 was the fine-tuned pH for whole electrochemical experiments. PY oxidation current decreases at acidic pH which may be due to protonation of pyridine group, and also after pH 6.5, the anodic current declines due to degradation of PY molecule forming the aldehyde-free radical.



**Fig. 5** a Sweep rate (0.1–0.250 V/s) studies of PY sensing at PAMCNTPE at optimal voltammetric parameters; b graphical plot of  $I_{pa}$  vs.  $v^{1/2}$



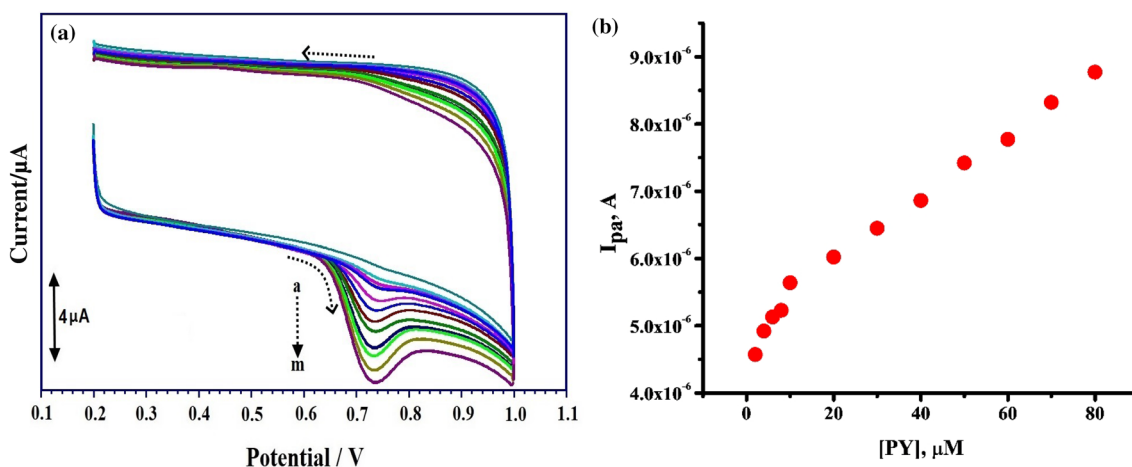
**Fig. 6** **a** Cyclic voltammograms for influence of pH (5.5–7.5) for PY sensing at PAMCNTPE with the sweep rate 0.1 V/s. **b** Plot oxidation peak current vs. solution pH values

### 3.7 Analytical Performance of PAMCNTPE

CV responses were used to quantify PY at PAMCNTPE in 0.1 M PBS solution of pH 6.5 with a 0.1 V/s sweep rate. Under calibrated conditions, the anodic peak current of PY as a function of concentration was investigated, as shown in Fig. 7a. The electrooxidation peak current is linearly proportional to the concentration over a range 10–80 μM (Fig. 7b); actually, the two linear curves are obtained between 2–10 and 10–80 μM, but we considered the fine linear 10–80 μM with linear equation  $I_{pa} \text{ (A)} = 5.2 \times 10^{-6} + 0.043 C \text{ (M)}$  with correlation coefficient ( $R$ ) of 0.99. The LOD is estimated to be  $9.6 \times 10^{-7}$  M and LOQ is  $3.21 \times 10^{-6}$  M with a sensitivity 0.04361 A/M. The LOD and LOQ was evaluated as  $LOD = 3SD \text{ (blank)}/S_C$  and  $LOQ = 10SD \text{ (blank)}/S_C$  [28], the SD (blank) is the

standard deviation of the blank (five measurements), and  $S_C$  is the slope of standard calibration graph.

Table 1 [29–35] compares the PAMCNTPE with other modified electrodes which are previously reported in the literature for sensing PY. The detection limit of  $9.6 \times 10^{-7}$  M of the proposed sensor is lower than that of disposable screen-printed electrode/CNTs [29], silver-doped poly(arginine)/GCE [30], boron-doped diamond electrode [31], vanadyl (IV)–salen complex-modified carbon paste [32] and close to screen-printed electrode/Ru nanoparticle [34], and graphene/ZnO nanocomposite [35], higher than the complicated preparation such as GCE/Au-CuO/MWCNTs [33]. This method provides a simple, disposable, and effective sensor for the PY determination in the presence of RF.



**Fig. 7** **a** Calibration curves for quantification of PY (2–80 μM) under optimal conditions, and **b** calibration plot of concentration of PY vs. oxidation peak current responses

**Table 1** Comparison of previously reported sensors with projected sensor for the determination of PY

Electrochemical sensors	Modifiers	Concentration range ( $\mu\text{M}$ )	LOD ( $\mu\text{M}$ )	Method of analysis	Reference
Disposable screen-printed electrodes	CNTs <sup>a</sup>	0.72–2.0	1.5	DPV <sup>b</sup>	[29]
Glassy carbon electrode	Silver-doped poly(arginine)	10–3000	5.0	LSV <sup>c</sup>	[30]
Boron-doped diamond electrode	–	7–47	3.76	DPV <sup>b</sup>	[31]
CPE <sup>d</sup>	Vanadyl (IV)–salen complex	450–3300	4.25	LSV <sup>c</sup>	[32]
Glassy carbon electrode	Au–CuO/MWCNTs <sup>e</sup>	0.79–18.4	0.150	DPV <sup>b</sup>	[33]
Screen-printed electrode	Ru nanoparticles MWCNTs	2.6–200	0.8	DPV <sup>b</sup>	[34]
Graphene	ZnO	1–1600	0.72	SWV <sup>f</sup>	[35]
CNTPE	Poly(arginine)	2–10 and 10–80	0.96	CV <sup>g</sup>	Present work

<sup>a</sup>Carbon nanotube tubes<sup>b</sup>Differential pulse voltammetry<sup>c</sup>Linear sweep voltammetry<sup>d</sup>Carbon paste electrode<sup>e</sup>Gold and copper oxide core shell/multiwalled carbon nanotubes<sup>f</sup>Square-wave voltammetry<sup>g</sup>Cyclic voltammetry**Table 2** PY estimation in real sample and recovery assessment

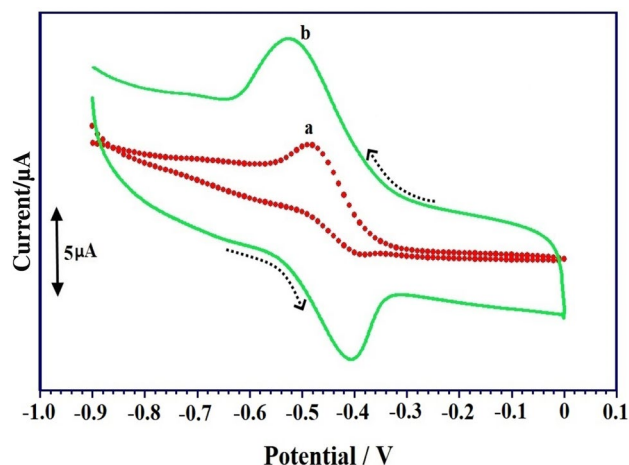
Sample	Added ( $\mu\text{M}$ )	Detected ( $\mu\text{M}$ )	Recovery (%)
Natural food supplement	10.0	9.7	97.0
	20.0	20.03	100.1

### 3.8 Analytical Applications

The devised sensor PAMCNTPE was applied to analyze PY in natural food supplement under optimized conditions using CV. The PY containing sample is dissolved in 0.1 M PBS (pH 6.5) to a known concentration of PY. The PY estimation was performed by standard addition strategy. The PAMCNTPE detects and quantifies the PY in natural food supplement with excellent recovery from 97.0% to 100.1% with RSD 1.27%. These results shows the analytical applicability of the proposed sensor (Table 2).

### 3.9 Estimation of Repeatability, Reproducibility, and Stability

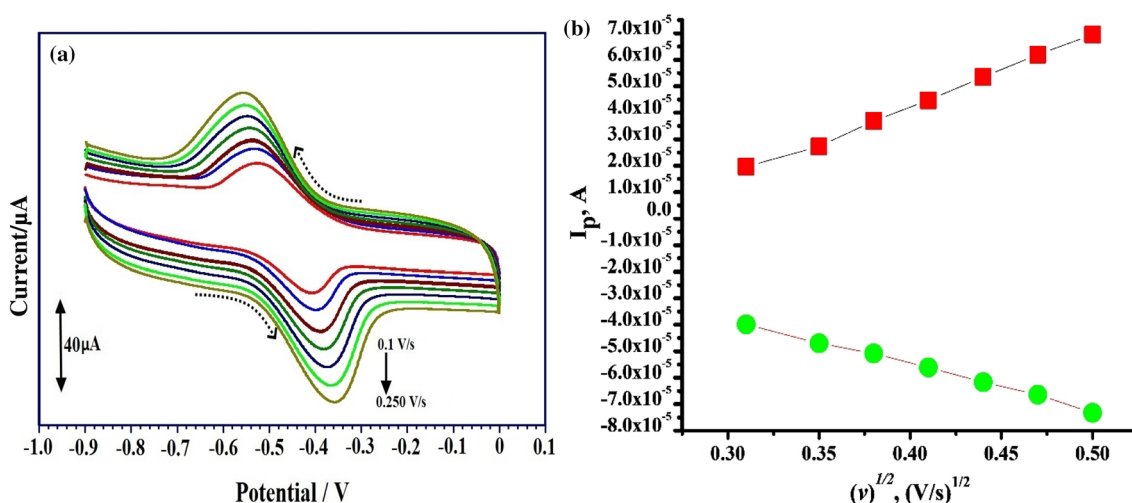
The repeatability, reproducibility, and stability in sensing the PY were estimated by CV under optimal conditions. Good repeatability was obtained for five consecutive measurements with RSD 1.2% and excellent reproducibility for five separate measurements was attained by the renewal of electrode with RSD 2.9%. Stability was studied by running 20 cycles continuously with 90% of primary current and potential signals were retained even after 20 cycles.



**Fig. 8** RF (0.1 mM) cyclic voltammetric response at BCNTPE (curve a) and PAMCNTPE (curve b) in PBS, pH 6.5 at sweep rate 0.1 V/s

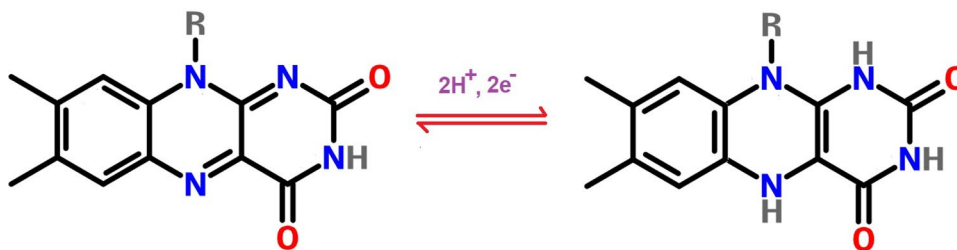
### 3.10 Cyclic Voltammetric Response of RF

The redox nature of RF (0.1 mM) at BCNTPE (curve a) and PAMCNTPE (curve b) was deliberated by CV in 0.1 M PBS of pH 6.5 at a potential scan rate of 0.1 V/s as demonstrated in Fig. 8. The BCNTPE detects the RF (0.1 mM) oxidation at  $-0.383$  V and reduction at  $-0.486$  V with minor current responses. The PAMCNTPE has a marked effect in sensing 0.1 mM RF the anodic potential appeared at  $-0.407$  V and cathodic potential at  $-0.524$  V with enhanced current signals. The sensing of RF was accelerated at PAMCNTPE with  $\Delta E_p$  as 0.117 V, so the RF electroreduction was quasi-reversible.



**Fig. 9** a Cyclic voltammograms of scan rate studies of RF at 0.1–0.250 V/s in PBS of pH 6.5 at PAMCNTPE; b a plot of peak currents of RF vs. square root scan rate

**Scheme 2** Redox process of RF

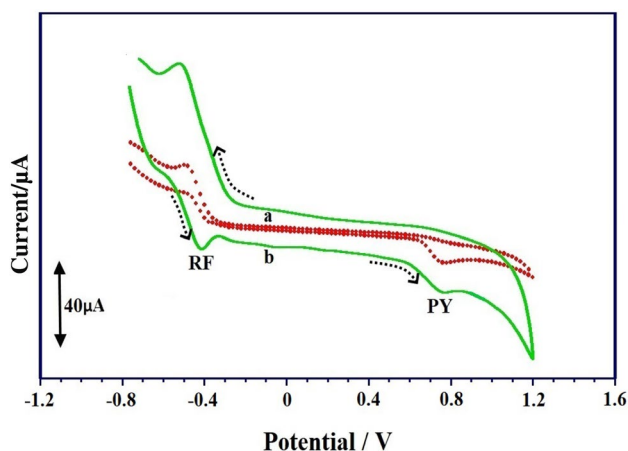


### 3.11 Influence of Sweep Rate

The sweep rate analysis from 0.1 to 0.3 V/s for RF detection was performed using cyclic voltammetry in 0.1 M PBS of pH 6.5 at PAMCNTPE, as shown in Fig. 9a. As the sweep rate increases, the anodic and cathodic current signals also increase, and the cathodic and anodic potentials shift opposite to each other with an increase in  $\Delta E_p$  values, which shows that the RF reduction is quasi-reversible. The plot  $v^{1/2}$  vs oxidation and reduction peak currents of RF (Fig. 9b) shows a linear relationship by agreeing linear equations  $I_{pa}$  (A) =  $6.57 \times 10^{-5} + 2.70 \times 10^{-5} v^{1/2}$  (V/s) and  $I_{pc}$  (A) =  $1.38 \times 10^{-5} + 1.72 \times 10^{-4} v^{1/2}$  (V/s) with  $R=0.99$ . This illustrates the electrochemical probe in detecting RF was under diffusion controlled. The generally accepted reduction mechanism of RF is shown in the Scheme. 2.

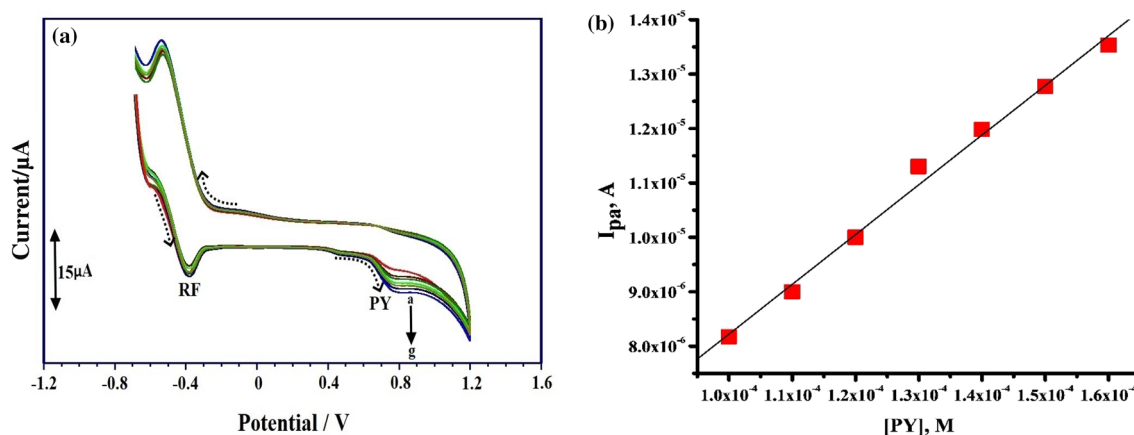
### 3.12 Concurrent Separation of RF and PY Using CV

The electrochemical separation of RF and PY was performed in the potential window  $-0.8$  to  $1.2$  V at PAMCNTPE (curve b) and BCNTPE (curve a) using CV in 0.1 M PBS of pH 6.5 at sweep rate 0.1 V/s, as shown in Fig. 10. The RF oxidation and reduction were sensed at  $-0.413$  V and



**Fig. 10** Simultaneous separation of RF and PY at BCNTPE (curve a) and PAMCNTPE (curve b) in PBS of pH 6.5 with 0.1 V/s sweep rate

$-0.525$  V, respectively, with excellent current responses and PY detected at  $0.771$  V with enhanced current responses with peak separation  $0.308$  V. In the case of BCNTPE, the RF anodic and cathodic peaks appeared at  $-0.376$  V and  $-0.501$  V, and PY was detected at  $0.772$  V with a low current response and peak separation  $0.396$  V. In the concurrent



**Fig. 11** **a** Cyclic voltammograms for concentration variation of PY from a to g, i.e., 0.1–0.16 mM in the presence of 0.1 mM RF under optimal conditions, and **b** a plot of PY addition vs.  $I_{pa}$

analysis, the RF reduction was quite sensitive than RF oxidation, because during the forward scan, the RF interacts less strongly may be due to interference of PY, but during a reverse scan, RF interacts more strongly with electrode yields more sensitivity for RF.

### 3.13 PY Variation in Presence of RF

The concentration variation of PY from 0.1 to 0.16 mM under optimal conditions was performed with the presence of 0.1 mM RF at PAMCNTPE using CV as revealed in Fig. 11a. At each successive increment in PY concentration is linearly proportional to the PY oxidation current without affecting much to RF peak characteristics. Moreover, the graphical plot of concentration variation PY vs.  $I_{pa}$  (Fig. 11b) gives excellent linearity with a coefficient of correlation 0.99.

### 3.14 RF Variation in Presence of PY

To check the detection ability of PAMCNTPE towards the detection of RF (0.1–0.15 mM) in the presence of 0.1 mM PY solution under optimal conditions using CV as demonstrated in Fig. 12a. The peak currents of RF vary linearly with each addition without affecting PY peak currents and potentials. This shows the possibility of determination RF in the presence of PY. The plot of peak currents of RF as a

function of RF addition gives a straight line with a correlation coefficient of 0.99 (Fig. 12b).

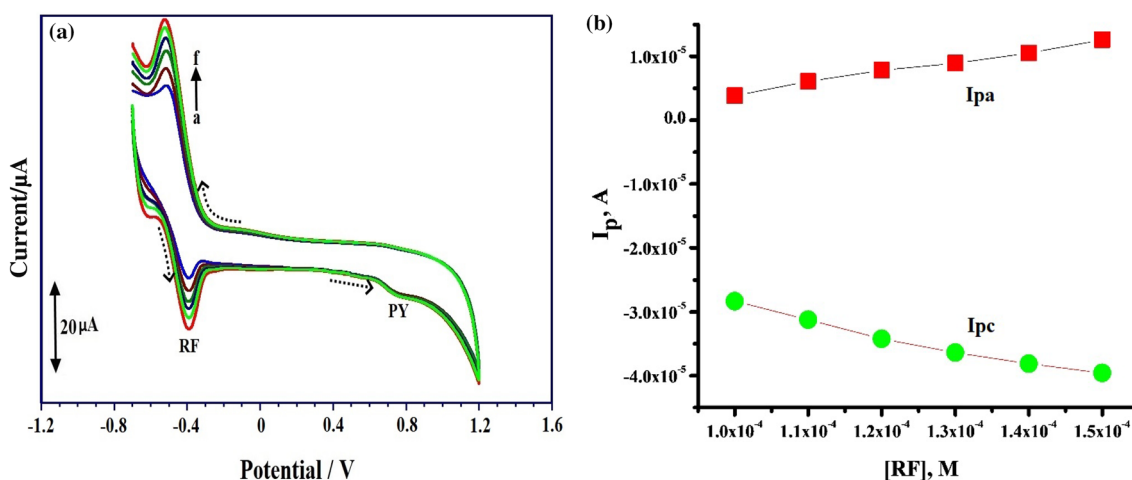
### 3.15 Interference

The common species that affect for PY sensing such as ascorbic acid, biotin, folic acid, riboflavin, tyrosine, estriol, uric acid, and glycine (0.1 mM) were examined under optimal conditions using CV and observed that there is no significant effect in detection of PY with these interfering molecules and limit of interference was below  $\pm 5$ . Therefore, the projected sensor exhibits excellent selectivity.

## 4 Conclusion

The simple and active electroanalytical sensor method is established for the determination of PY. The proposed sensor delivers excellent analytical performance after modification with poly(arginine) as compared to the unmodified electrode. The devised electrochemical sensor provides large effective area, and high electrical conductance through the polymer layer. Moreover, the fabricated sensor exhibits good repeatability, stability, simultaneous analyzing ability with less interference effect, effective analytical applications in pharmaceutical formulations. These excellent features make the developed sensor another alternative for the detection and quantification of PY.





**Fig. 12** **a** Cyclic voltammograms for concentration variation of RF from a to f, i.e., 0.1–0.15 mM in presence of 0.1 mM PY under optimal conditions, and **b** a plot of RF addition vs.  $I_{pa}$  and  $I_{pc}$

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### Compliance with ethical standards

**Conflict of interest** The authors declare no conflict of interest.

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