Polypyrrole-Pd nanocomposites modified gold electrode for electrochemical detection of ascorbic acid

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Abstract

The fabrication of an electrochemical sensor based on polypyrrole-Pd nanocomposites modified gold electrode (PPy-Pd-AuE) and its electrodetection of ascorbic acid is described. The PPy-Pd nanocomposites were synthesized by chemical method and characterized by different techniques. The Pd nanoparticles incorporated with PPy were confirmed by x-ray diffraction, scanning electron microscope, elemental dispersive spectroscopy and transmission electron microscopy analysis. The electrochemical behavior of polypyrrole-Pd nanocomposites towards the electro catalytic oxidation of ascorbic acid was investigated by cyclic voltammetry, differential pulse voltammetry and square wave voltammetry. The observed cyclic voltammetry, differential pulse voltammetry and square wave voltammetry response depended linearly on concentration of ascorbic acid in the range of 100-1000 μM with correlation coefficients of R^2=0.977, R^2=0.980, R^2= 0.990 and sensitivity 7.96 μA/μM.cm^2, 0.70 μA/μM.cm^2 and 2.10 μA/μM.cm^2 respectively. The reproducibility of PPy-Pd-AuE electrode from CV, DPV and SWV were found to be 3.9%, 4.69% and 2.98 % respectively. These results indicate the PPy-Pd-AuE exhibited excellent platform and could be used for electrochemical determination of ascorbic acid. Copyright © 2017 VBRI Press.

Keywords: Pd- Nanoparticles; PPy-Pd nanocomposites; electrochemical analysis; ascorbic acid sensor.

Introduction

L-ascorbic acid (vitamin C) is a well-known antioxidant, which helps the human body in preventing oxidation process which causes tissue damage [**1-2**]. Ascorbic acid is an important water soluble vitamin helping human body in producing collagen, a protein which is useful for the development and maintenance of structure of bones, cartilage, joint linings, teeth muscles and blood vessels [**3-5**]. The most of the animals can synthesize vitamin C from D-glucose with the help of enzyme 1-gulono-gamma-lactone oxidase required for the termination step in biosynthesis of vitamin C. But gulo-gene is inactive in the human body and cannot produce ascorbic acid, so we need to take it from diet [**6**]. The diet enriched with ascorbic acid is prescribed as supplement to the patient of Cancer and AIDS [**7**]. It involves in many biochemical functions as a cofactor for several enzymes in synthesis of adrenal hormones, metabolism of folic acid, tyrosine and tryptophan [**8-9**]. It also involves in iron absorption, activation of immune response and also participating in wound healing and osteogenesis. The deficiency of ascorbic acid causes scurvy while excess ascorbic acid causes gastric irritation and renal problems [**10**].

Here determination of ascorbic acid in its solution is more important. Many analytical methods have been reported for the determination of ascorbic acid such as conventional titration [**11**], HPLC [**12**], spectrophotometry [**13**], enzymatic analysis [**14**] and capillary electrophoresis [**15**]. These methods are relatively time consuming, have less selectivity, less stability and expensive.

The electrochemical method is widely applied for the determination of ascorbic acid since it is simple, sensitive and moderate. The electrochemical techniques such as cyclic voltammetry (CV) [**16-17**], square wave voltammetry (SWV) [**18**], differential wave voltammetry (DPV) [**19**] and amperometric [**20**] are useful for detection of ascorbic acid. The evaluation of ascorbic acid was done by direct electrooxidation at conventional electrodes, such as Hg [**21**], Au [**22**], Pt [**23**] and glassy carbon electrode (GCE) [**24**]. The examination of ascorbic acid on these electrodes is quite problematic due to the fouling effect on the electrode surface by oxidation [**25**]. This problem is solved by surface modification of electrode by various techniques. The electrochemical analysis study show that various nanocomposites materials have been used as modified electrode such as AgNps-rGO [**17**], Cu Nps-PSA [**26**], ZnO-rGO [**19**], SWCNT/ZnO [**27**] and Fe_3O_4/rGO [**28**]. Recently there has been wide interest in the field of conducting polymer modified electrode as it exhibits more porous structure.

Among the conducting polymers, polypyrrole (PPy) has good mechanical and chemical stability, easy preparation and is most promising member for application in electrocatalytic as well as other purposes [**29-30**]. PPy has been successfully applied as conducting matrix of composite material incorporating with SeO_2 [**31**], CeO_2 [**32**], GaN [**33**], Co [**34**] and noble metals such as Au [**35**], Ag [**36**], Pd [**37**] and Pt [**38**].

The study of chemically synthesized PPy-Pd nanocomposites for the electrochemical detection of ascorbic acid has received less attention. Electrochemical detection is an attractive alternative method for detection of electroactive species, because of its inherent advantages of simplicity, ease of miniaturization, high sensitivity and relatively low cost. In the present observation we have adapted electrochemical detection of ascorbic acid by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV) techniques.

Experimental

Materials

Pyrrole (Spectrochem), ferric chloride (SD-Fine Chem.), palladium (II) Acetate (Alfa Aesar), L-Ascorbic acid (SD Fine), KCL(Sigma -Aldrich) and Nafion-D 521 dispersion (Alfa Aesar) were purchased and use as such as without further purification. All solutions were prepared in double distilled water.

Green synthesis of Pd nanoparticles

The honey solution was prepared by dissolving 1 g of honey in 100 ml of distilled water. In reaction flask the 50 ml honey solution was heated for 20 min at 80°C. Palladium acetate (0.01M) 50 ml solution was added drop wise into the preheated honey solution. The mixture solution was stirred with high speed for 6 hrs at 80°C. The resulting solution changed the color from colorless to brown and finally black color precipitate formed which was indicated formation of Pd nanoparticles. The colloidal solution of Pd nanoparticles was centrifuged at 6000 rpm for 2 hrs The obtained Pd nanoparticles were washed 2-3 times with distilled water and also with acetone and dried in vacuum desiccator. The dried Pd nanoparticles were store at ambient temperature in air tight glass container.

Synthesis of PPy- Pd nanocomposites

The doping of PPy was done by addition of 500 mg Pd nanoparticles in pyrrole solution. The solution was stirred for 30 min at 5ºC [**39**] and $FeCl_3$ oxidant was added dropwise to polymerize the reaction. The ratio of monomer (pyrrole): oxidant ($FeCl_3$) was 1:2.4[**40**]. The resulting mixture was stirred for 4 hours. The solution was kept unagitated for 24 hours so that Ppy-Pd nanocomposite powder settled down. The PPy-Pd crystals were filtered out under vacuum, washed with distilled water and with acetone 3-4 times to remove impurities if any. The PPy-Pd nanocomposites were dried for 2 days at room temperature. The dried PPy-Pd nanocomposites were stored at ambient temperature in air tight glass container.

Preparation of modified electrode

The gold (Au) electrode (2 mm diameter) was carefully polished using a polishing cloth with alumina slurry and then rinsed thoroughly with glass distilled water. The Au electrode was placed in ultrasound cleaner for 5 min, rinsed again with glass distilled water and allowed to dry at RT. To prepare the Au electrode modified with PPy-Pd nanocomposites, an alcoholic solution of 0.1 % Nafion D 251 dispersion of PPy-Pd nanocomposite (1mg mL^{-1}) was prepared and the suspension (5μL) was cast on to the surface of pretreated Au electrode. The solvent was allowed to evaporate at RT which resulted in immobilized PPy-Pd nanocomposites material on the Au electrode surface.

Characterization

The prepared materials of Pd nanoparticles and Ppy-Pd nanocomposites were characterized by FT-IR, XRD, TEM and SEM techniques. The IR spectrum was recorded on FT-IR spectrophotometer [JASCO, FT-IR/4100] Japan using dry KBr as standard reference in the range of 400–4000 cm.$^{-1}$ The X-ray powder diffraction patterns of the Pd nanoparticles and Ppy-Pd nanocomposites were recorded on Bruker 8D advance X-ray diffractometer using CuKα radiation of wavelength = 1.54056 Å. To study the- morphology and composition, Pd nanoparticles and Ppy-Pd nanocomposites were examined using SEM-EDS. The SEM analysis was carried out with JEOL; JSM- 6330 LA operated at 20.0kV and 1.0000nA. Shape, size, morphology was calculated by TEM analysis carried out on Philips model CM200 operated at 200kV.

Electrochemical analysis

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV) measurements were performed on a Metrohm Autolab PGSTAT128N (Metrohm B.V., Utrecht, Netherlands). A compartment consists of three electrode system containing, a saturated Ag/AgCl reference electrode, a platinum wire auxiliary electrode and a modified Au electrode as working electrode. Ascorbic acid measurement was carried out in 0.1 M KCl at room temperature. The CV, DPV and SWV were done at different concentration of ascorbic acid in the range 100 μM to 1000 μM at100 mVs^{-1}. For CV measurements, the potential scan was taken from -0.60 to 1.0 V at the different scan rate in the range 25-150 mVs^{-1}.

Results and discussion

Fourier transforms infrared (FTIR) spectroscopy

The FTIR spectrum of Pd nanoparticles observed in **Fig. 1a** show peaks at 3427 $cm^{-1}$and 1631 cm^{-1} due to stretching and bending mode of vibration of –OH groups respectively as absorption of water takes place on the sample due to contact with environment. The peaks observed at 592 cm^{-1}, 470cm^{-1} and 433cm^{-1} corresponds to Pd-Pd and Pd-O bending mode of vibration. **Fig.1(b)** shows peaks of PPy-Pd nanocomposites at 3427 cm^{-1}due to N-H stretching of PPy. Peaks at 2922 cm^{-1} and 2848 cm^{-1} can be assigned to C-H stretching. Peak at 1631 cm^{-1}, 1525 cm^{-1} & 1445 cm^{-1} correspond to fundamental vibration of polypyrrole ring. The characteristic peaks due to the PPy component at 1370 cm^{-1}, 1142 cm^{-1}, 1016 cm^{-1}, 498 cm^{-1} and 445 cm^{-1} were obtained which indicate the existence of PPy-Pd nanocomposites in the composites particles.

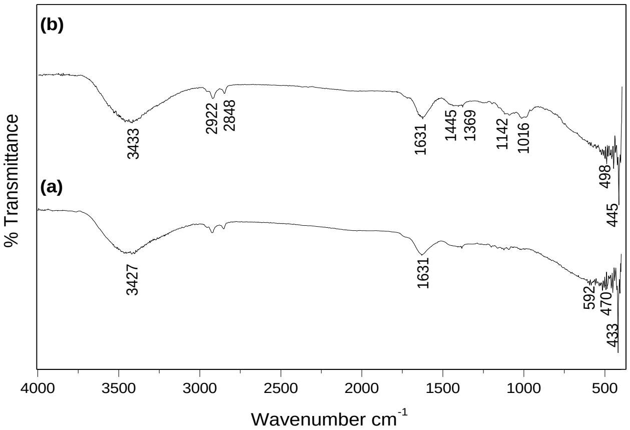

Fig.1 FTIR spectra of (a) Pd Nps and (b) PPy-Pd nanocomposites

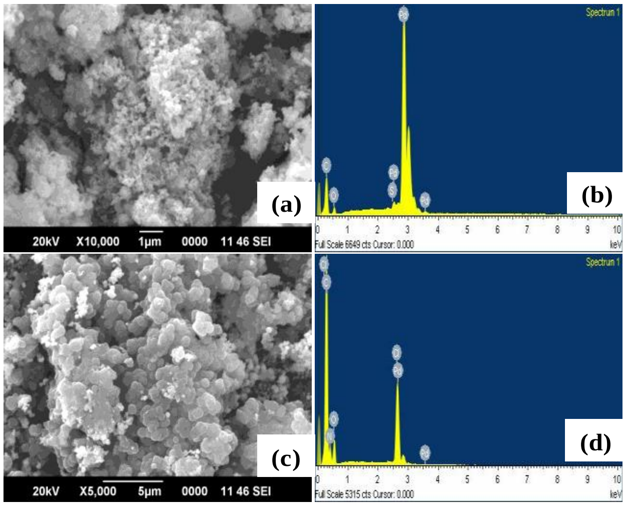

Fig. 2 SEM images of (a) Pd Nps, (c) PPy-Pd Nanocomposites and (b) and (d) respective EDS spectra.

Scanning electron microscopy (SEM)- Energy dispersive spectroscopy (EDS)

To evaluate morphology of Pd nanoparticles and PPy-Pd nanocomposites, SEM analysis were carried out. The SEM micrograph of Pd nanoparticles in **Fig. 2a** showed the spherical structure, agglomeration and highly porous nature of Pd nanoparticles. **Fig. 2c** clearly shows Pd nanoparticles agglomeration with Pyrrole to form porous PPy-Pd nanocomposite. The composition of prepared Pd nanoparticles and PPy-Pd nanocomposites were analyzed qualitatively and quantitatively by EDS. From **Fig. 2b** the weight % found to be carbon 9.62%, oxygen 5.85 % and Pd 84.25 % composition of Pd nanoparticles. In **Fig. 2d** weight % found that carbon 64.77 %, nitrogen 14.65 %, oxygen 12.76 and palladium 6.75% composition which confirmed the formation of PPy-Pd nanocomposites.

Transmission electron microscope (TEM)

The TEM micrographs depicted in **Fig. 3a, 3c** is direct morphological observations of Pd nanoparticles and Ppy-Pd nanocomposites. The average overall dimensions of Pd nanoparticles and PPy-Pd nanocomposites were 10-20 nm and 5-20nm respectively. The shape of Pd nanoparticles was spherical while PPy-Pd nanocomposites clearly showed Pd nanoparticles deposited on porous polypyrrole. **Fig. 3b** and **Fig. 3d** show SAED pattern of Pd nanoparticles and PPy-Pd nanocomposites respectively which shows spotty ring indicating crystalline nature of nanocomposites.

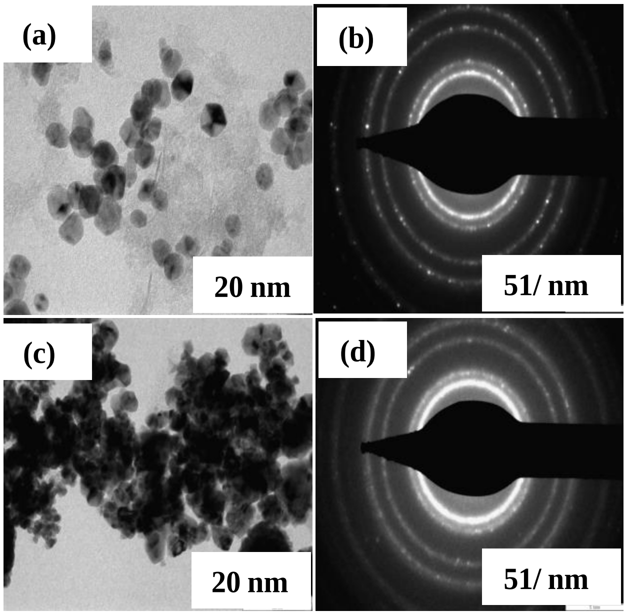

Fig. 3 TEM images of (a) Pd Nps (c) PPy-Pd nanocomposites and (b) & (d) respective SAED patterns.

Cyclic voltammetry

In order to investigate the electrocatalytic oxidation activity of PPy-Pd modified AuE in 0.1 M KCl solution, the CV results were studied in presence and absence of 200 µM of ascorbic acid in 0.1 KCl at scan rate 100mV/s in potential range of -0.6V to 1.0V. The CV recorded in the 0.1 M KCl with 200 µM ascorbic acid is presented in **Fig. 4a**. The scanning mechanism involves the ascorbic acid molecules adsorbed onto the surface of PPy-Pd-AuE. The ascorbic acid molecules were hydrolyzed with water and oxidized to dehydroascorbic acid. This oxidation process of ascorbic acid can release electrons that correspond to current which can be detected. It was observed that the oxidation of the ascorbic acid is an irreversible process due to the absence of a reduction peak.

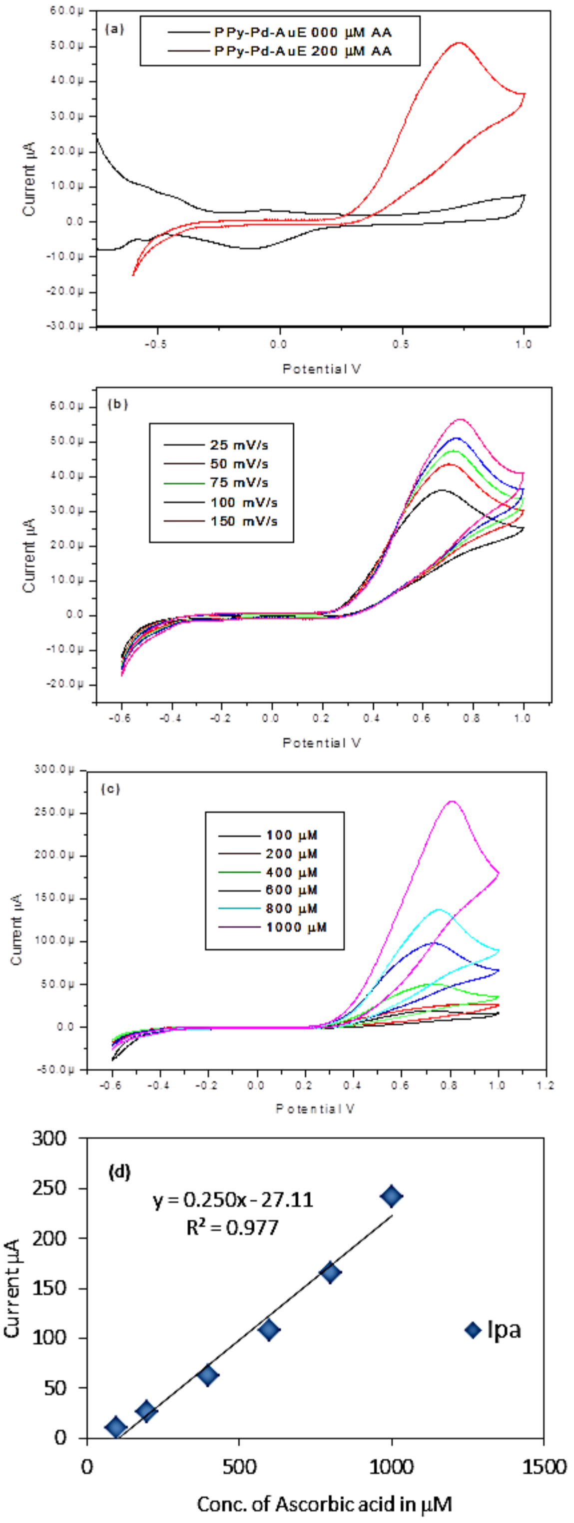

Fig. 4 a) CV of without (black) and with (red) 200 µM of ascorbic acid in 0.1 KCl solution of scan rate 100 mV/s at Pt-PPy-PtE. b) CV response of 200 µM of ascorbic acid in 0.1 KCl solutions at different scan rate 25-150 mV/s at PPy-Pd-AuE. c) CV response of PPy-Pd-AuE electrode in 0.1 KCl solutions containing 100 µM to 1000 µM of ascorbic acid at scan rate 100mV/s. d) Linear regression curve for concentration of ascorbic acid vs. peak current.

Cyclic voltammetry response of 200µM ascorbic acid in 0.1 KCl modified PPy-Pd-AuE at different scan rate from 25mV/s to150 mV/s in potential range -0.6 to 1.0V is seen in **Fig. 4b**. **Fig. 4c** shows the obtained cyclic voltammetry at PPy-Pd-AuE electrode for different concentration of ascorbic acid varied from 100 µM to 1000 µM. The increase in peak currents is largely the result of increased electroactive surface area of the PPy-Pd-AuE. The oxidation peak current obtained was directly proportional to the concentration of AA plotted in **Fig. 4d**, from the linear regression equation R^2= 0.977 and the sensitivity were found to be 7.96 µA/µM.cm^2.

Differential pulse voltammetry (DPV)

DPV is often used to make electrochemical measurements. The current is measured immediately before each potential change, and the current difference is plotted as a function of potential. By sampling the current just before the potential is changed, the effect of the charging current can be decreased. The differential pulse voltammetry (DPV) was developed for the detection of ascorbic acid. **Fig. 5a** shows the obtained differential pulse voltammograms at PPy-Pd-AuE for different concentration of ascorbic acid. The concentration was varied from 100 µM to 1000 µM in 0.1 KCl. The ascorbic acid oxidation peak current obtained was directly proportional to the concentration of AA was plotted as can be seen in **Fig. 5b**, from the linear regression equation R^2= 0.980 and the sensitivity were found to be 0.70 µA/µM.cm^2.

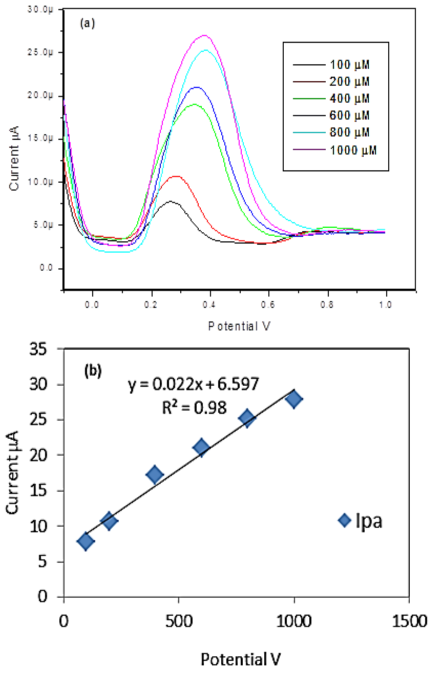

Fig. 5 a) Differential Pulse voltammetry (DPV) response of PPy-Pd-AuE electrode in 0.1 KCl solutions containing 100 µM to 1000 µM of ascorbic acid. b) Linear regression curve for concentration of ascorbic acid vs. peak current.

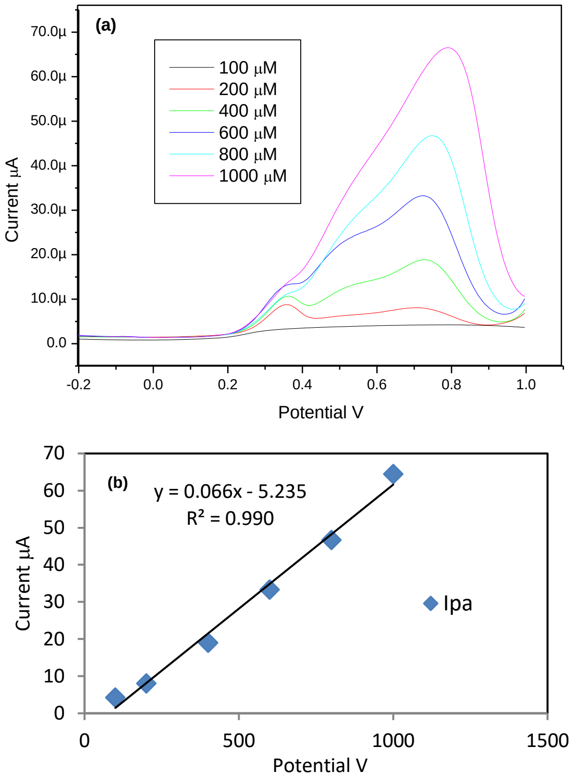

Fig. 6 a) Square Wave voltammetry (SWV) response of PPy-Pd-AuE electrode in 0.1 KCl solutions containing 100 µM to 1000 µM of ascorbic acid. b) Linear regression curve for concentration of ascorbic acid vs. peak current.

Table 1. Comparative study of various modified electrode acts as electrochemical detection of ascorbic acid.

Modified electrode	Technique	Linear range (µM)	Sensitivity	Ref.
Graphene ceramic composite	CV	3-84	6.06 µA/µM-cm^2	**[41]**
Ag Np/rGO	CV	0.11-600	101.86 µA/µM-cm^2	**[17]**
SWCNT/ ZnO	CV	200-1000	13.7 µA/mM-cm^2	**[27]**
Chitoson Graphene-GCE	DPV	0.6-1678	9.344 µA/µM-cm^2	**[42]**
GO-Temp-PANI microsheet	DPV	150-1050	10.88 µA/µM-cm^2	**[19]**
CTAB-GO-MWNT-GCE	DPV	5-300	401.64 µA/µM-cm^2	**[38]**
Fe_3O_4/rGO/GCE	DPV	0.5-100	2.733 µA/µM-cm^2	**[28]**
MWCNT/GCE	SWV	4.7-5000	0.471 µA/µM-cm^2	**[18]**
PPy-Pd/AuE	CV	100-1000	7.96 µA/µM-cm^2	This work
	DPV	100-1000	0.70 µA/µM-cm^2	
	SWV	100-1000	2.10 µA/µM-cm^2	

Square Wave Voltammetry (SWV)

The development of this technique allowed for the rapid collection of reliable and easily reproducible electrochemical data using working electrodes. With continued improvements from many electrochemists, SWV is now one of the primary voltammetric techniques available on modern potentiostats. The square wave voltammetry (SWV) was also studied for the electrochemical detection of ascorbic acid. **Fig. 6a** shows the obtained square wave voltammograms (SWVs) at PPy-Pd-AuE for different concentration of ascorbic acid. The concentration was varied from 100 µM to 1000 µM in 0.1 KCl. The ascorbic acid oxidation peak current obtained was directly proportional to the concentration of ascorbic acid as plotted and can be seen in **Fig. 6b**, from the linear regression equation R^2=0.990 and the sensitivity found to be 2.10 µA/µM.cm^2.

The comparative study of various modified electrode acts as electrochemical detection of ascorbic acid as shown in **Table 1**. Most of the reported modified electrodes have less sensitivity and shorter range of concentration. In this work, we have developed electrochemical sensor based on conducting polymer nanocomposites PPy-Pd-AuE for the determination of ascorbic acid. Using this system, we have been able to detect ascorbic acid over range of concentrations (100 µM to 1000 µM) with good sensitivity of CV (7.96 µA/µM-cm^2), DPV (0.70 µA/µM-cm^2) and SWV (2.10 µA/µM-cm^2). The reproducibility of PPy-WO_3-AuE was investigated by CV and DPV analysis in solution containing 200µM ascorbic acid in 0.1 KCl. For five different runs, the standard deviation was obtained from CV (3.90 %), DPV (4.69%) and SWV (2.98%), which indicate that the modified electrode can reproducibly determine the ascorbic acid.

Conclusion

In the present study, we have successfully synthesized PPy-Pd nanocomposites by chemical method. The PPy-Pd nanocomposites were crystalline, porous materials, Pd nanoparticles incorporated with polypyrrole and average size 5-20 nm, which resulted from SEM-EDS and TEM-SAED analysis. The PPy-Pd nanocomposites modified gold electrode was successfully used for detection of ascorbic acid. The CV, DPV and SWV curves showed that the concentration of ascorbic acid increased with the peak current and peak height [**43-44**]. The CV, DPV and SWV methods were successfully used for detection of ascorbic acid at PPy-Pd-AuE modified electrode which have good sensitivity and reproducibility.

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Author's contributions

Conceived the plan: Anjali S. Rajbhoj, Suresh T. Gaikwad; Performed the expeirments: Nitin R. Dighore; Data analysis: Nitin R. Dighore; Wrote the paper: Nitin R. Dighore, Anjali S. Rajbhoj, Suresh T. Gaikwad are the initials of authors. Authors have no competing financial interests.

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