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# Influence of Pd Nanostructures on The Redox Electrochemistry of Ferrocene Monocarboxylic Acid and Ferrocene for Ascorbic Acid Sensing

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Abstract- The effect of Pd nanoparticles geometry has been studied on modifying Fc and Fc-COOH-based electrodes. It has been found to have more reliable results before and after Pd use with Fc-COOH modified electrode. The sensing activity has been performed for ascorbic acid and found quite good results with Fc-COOH-based electrode and surprising results with Pd-modified Fc and Fc-COOH-based electrode, which is further confirmed by performing amperometry titration and observed much high current in case of PdNPs modified Fc-COOH based electrode. The rise in anodic peak current from 14.5µA to 33.01µA and 1.30 µA to 3.63 µA for Fc and Fc-COOH modified electrodes under a similar environment. The current function continuously rises from 10 to  $16 \,\mu A/(mV)^{0.5}$  and 6.5 to  $13.4 \,\mu A/(mV)^{0.5}$ . The R<sub>ct</sub> value decreases from 12.8 k $\Omega$  to 1.9 k $\Omega$  and 8.3 k $\Omega$  to 1.5 k $\Omega$ , respectively. Electrochemical impedance spectroscopy has also been studied, confirming that PdNPs modified Fc and Fc-COOH-based electrodes having low R<sub>ct</sub> value, the faster charge transfer is compassionate toward ascorbic acid. Transmission electron microscopy, PXRD, and CV have all been used to characterize the nanomaterial with the following major investigation:(i) The average size of PdNPs-1& PdNPs-2 is found 18 nm & 8 nm, (ii) It has been discovered that the palladium content influences both the electrocatalytic effectiveness of novel modified electrode materials and the oxidoreduction electrochemistry of ferrocene and Fc-COOH, and(iii) The modified electrode has an extremely low detection limit for ascorbic acid of  $<5 \mu$ M.

**Keywords-** Palladium nanoparticles; Cyclic Voltammetry; Amperometry; Electrochemical Impedance spectroscopy

# **1. INTRODUCTION**

Several studies have been made on electrochemical biosensors during the last four decades [1]. The creation of mediator-based electrochemical sensors has made use of redox mediators. Numerous studies have been done using ferrocene and its derivatives as effective electrocatalysts. Because it is an excellent organometallic one-electron reservoir and one of many redox mediators, ferrocene (Fc) is a popular electroactive molecule [2,3]. Fc-modified surfaces have consistently perfect electrochemical properties and have outstanding electrochemical stability, according to cyclic voltammetry measurement. Pd-modified Fc-based materials offer versatile electrochemical applications due to synergistic effects [4].

The reversible oxidation of air- and water-stable ferrocene to  $Fc^+$  makes it an excellent internal standard in electrochemistry. In general, ferrocene's chemical and physical properties and its derivatives can be used in a broad range of applications, including sensing, materials research, and catalysis [5]. Under mild potential conditions, the ferrocenium ion (Fc<sup>+</sup>) is generated from ferrocene (Fc) via a reversible oxidation process. Due to this characteristic, ferrocene is perfect for usage in supramolecular systems that require straightforward redox chemicals at the surface of the electrode. Most forms of ferrocene satisfy each ideal redox mediator's requirements: production of stable redox forms, reversibility, regeneration at low potential, low molecular mass, lack of pH dependence, and absence of oxygen reaction [6].

Ascorbic acid (AA) is a crucial nutrient for people and is found in both the animal and plant worlds, where it plays a vital role in cellular metabolism. It aids in the growth of new cells, the recovery of wounds and burns, and the production of collagen, blood vessels, bones, cartilage, and tendons [7]. Among other things, fruits and vegetables are the primary sources of the water-soluble substance ascorbic acid. It is well-known for its medicinal use, antioxidant impact on foods and beverages, and reductive capabilities. To oxidize ascorbic acid in an aqueous solution, chemically modified electrodes with a variety of active mediators immobilized at the electrode surfaces were used. On the other hand, an overdose of AA can cause chemical conversion into oxalate, contributing to an increase in the level of oxalate in urine and, in the long run, the development of kidney stones [8].

AA has been detected in biological fluids, food, and pharmaceutical formulations using spectroscopy, chromatography, chemiluminescence, optical sensors, and electrochemical methods. Electrochemical methods receive a lot of interest due to their quick reaction, easy instrumentation, high sensitivity, compactness, in vivo detection capabilities, low cost, and ease [9,10].

It has also been shown that the alkyl chain connected to the amine group affects how easily NPs disperse in organic and aqueous media. Furthermore, the functional ability of organic amine attached to the alkoxysilane group enables the usage of 3-APTMS for altering nano shape, functional ability, dispersibility, and processability in a single step, which facilitates the synthesis of AuNPs, PdNPs, and Au-Pd/Pd-Au [11,12].

Pd-Fc/Fc-COOH activity is recognized by using 3-APTMS and organic reducing agents such as cyclohexanone/formaldehyde, introducing another effective method for controlling nanoparticle synthesis and catalytic activity. For two fundamental reasons, Fc/Fc<sup>+</sup> evolved into the redox couple that epitomizes organometallic electrochemistry; 1) Quick and kinetically straightforward, the ferrocene self-exchange process, and 2) its rate is not affected by the solvent. At the solid electrode, the heterogeneous electron transport is electrochemically reversible, comparably fast, and not hampered by homogeneous processes [13]. Numerous ferrocene derivatives satisfy the requirements for ideal redox mediators, including (a) reversibility, (b) regeneration at minimal potentials, (c) low molecular mass, (d) consistency of each form of the redox couple, and (e) insensitivity to pH consistency of each form of the redox couple [2].

Carbon paste electrodes have been one of the most common microporous matrixes for exploring mediated bioelectrochemistry. Two mixtures of hydrophobic and hydrophilic alkoxysilanes, such as (1) GPTMS, (2) 3-APTMS and EETMS, were used at an inadequate ratio to encapsulate ferrocene and ferrocene monocarboxylic acid (Fcmc). When the Fc, Fc-COOH was encapsulated within an ormosil film made from palladium linked-GPTMS and 3-APTMS, the reversible electrochemistry of the Fc, Fc-COOH was excellent, even more adequate than the exact measurement made in a homogeneous solution. When used in controlled bioelectrochemical sensing, the nano shape thin film was able to speed up the regeneration of redox enzymes [14-17].

The aim of the present work is to investigate the following; 1) Effect of the shape of Pd nanoparticles on the bioelectrochemistry of Fc and Fc-COOH, (2) to better understand how nano-shaped palladium and Fc, Fc-COOH modified electrodes work as electrocatalysts, (3) the interaction of organotrialkoxy silane with the nanostructured Pd and Fc and Fc-COOH.

#### 2. EXPERIMENTAL SECTION

#### 2.1. Materials

Ferrocene (Fc), Ferrocene monocarboxylic acid (Fc-COOH), graphite powder (particles size  $<20 \mu$ m), Nujol oil (density0.838 g/ml), K<sub>2</sub>PdCl<sub>4</sub>, were obtained from Sigma Aldrich Chemical Co. India. Ascorbic acid, Anhydrous sodium phosphate (Na<sub>2</sub>HPO<sub>4</sub>), and Dihydrogen sodium phosphate mono hydrates (NaH<sub>2</sub>PO<sub>4</sub>.H<sub>2</sub>O) were obtained from HiMedia Chemicals, India. 3-Aminopropyltrimethoxysilane (3-APTMS) and 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (EETMS) get received from TCI India. All other chemicals used were of analytical grade.

#### 2.2. Synthesis of Palladium Nanoparticles (PdNPs)

**PdNPs-1**-The Palladium nanoparticles have been synthesized by the previously reported method [18], which involves mixing of methanolic solution of  $K_2PdCl_4(10 \text{ mM})$  80 µl,

Polyvinyl pyrrolidone (PVP 1%) 20  $\mu$ l and EETMS (10 mM) 20  $\mu$ l. Stirred the solution on cyclo mixture and kept in the oven for 5-10 minutes for incubation at 40-50 °C. The brownish-black colloidal solution is obtained and represented as PdNPs

**PdNPs-2-** 50  $\mu$ L methanolic solution of 10 mM of K<sub>2</sub>PdCl<sub>4</sub> was premixed with 10  $\mu$ L of methanolic solution of 3-APTMS (0.5-4 M) stirred for 2 minutes, followed by the addition of 50  $\mu$ L formaldehyde. The solution was kept under the microwave oven for incubation for 70 seconds. The black colloidal solution was obtained [19].

#### 2.3. Measurement and Characterization

Transmission electron microscopy (Tecnai G2 20 TWIN, FEI Electron Optics) was used to analyze the shapes and sizes of palladium nanoparticles. The synthesized Pd nanoparticles were confirmed by powder XRD (Rigaku mini flex 600 Japan).

# 2.4. Preparation of Carbon Paste Modified Electrode (CPE)

Palladium nanoparticles (PdNP-1 & PdNP-2) were adsorbed on graphite powder as they were produced. Pd nanoparticles with graphite were made by mixing 100  $\mu$ l Pd nanoparticle sol with 100 mg graphite powder (particle size 2-20  $\mu$ m) and ultrasonicated for 30 minutes. To ensure complete drying, the mixtures were kept at 60 °C overnight. To remove the organic functionality of the Palladium nanoparticles accumulated on graphite were calcined at 500 °C in an N<sub>2</sub> gas environment. In a grinder, the solid residues (which contained Palladium nanoparticles adsorbed on graphite powder) were mixed entirely with Ferrocene and Ferrocene monocarboxylic acid (Fcmc).

The presence or absence of Pd nanoparticles in the active paste led to the production of modified graphite paste electrode (GPE) systems such as GPE/Fc, GPE/Fcmc, GPE/Fc-PdNP-1, GPE/Fcmc-PdNP-2, and GPE/Fcmc-PdNP-2. The borosilicate glass capillaries were used to fabricate the carbon paste electrode. The well of the electrode was filled with a modified carbon paste containing the ingredients shown in Table 1.

System	Fc/Fc-COOH (w/w%)	PdNPs adsorbed on graphite(w/w%)	Graphite (w/w%)	Nujol oil (w/w%)
Fc/Fc-COOH	2.0	-	68	30
Fc-PdNP-1/ Fc-COOH-PdNP-1	2.0	10	58	30
Fc-PdNP-2/ Fc-COOH-PdNP-2	2.0	10	58	30

 Table 1. Composition of the mediator-modified electrode

### 2.5. Electrochemical Measurement

The electrochemical experiments were recorded using a computer-controlled electrochemical workstation Model CHI 660B TX, USA. Using an experimental setup where the resistance was gradually compensated for the uncompensated state, each CV was recorded many times. Using a three-electrode cell setup with a working capacity of 3 mL, the measurements were performed. An Ag/AgCl electrode (RE1B, ALS co.-Japan) and a Pt foil electrode are used as reference and counter electrodes. All potentials given below were relative to the Ag/AgCl. The modified carbon paste electrode was used as a working electrode. Analysis of the effect of sweep rates on peak current density was carried out by recording cyclic voltammograms at different scan rates starting at  $0.01 \text{ Vs}^{-1}$  to  $0.5 \text{ Vs}^{-1}$ . AA was detected using cyclic voltammetry, DPV, and amperometry in a 0.1 M phosphate buffer (pH 7.0) with 0.5 M KCl. Freshly prepared AA was used for all experiments. All the experiments were performed at ambient temperature and under similar conditions.

# **3. RESULTS AND DISCUSSION**

### 3.1. Characterization of Pd Nanoparticles

The current study displays the usage of two different sizes of palladium, i.e., PdNP-1 and PdNP-2, to investigate their effects on the oxidation & reduction electrochemistry of Fc-COOH and Fc.



**Figure 1.** TEM image (a,d), SAED pattern (b,e), and histogram (c,f) of the PdNPs-1 & PdNPs-2, respectively

Figure 1(a,d) shows the TEM examination of PdNP-1 and PdNP-2. The PdNPs nanosphere and hexagonal, triangular form are clearly seen in the TEM pictures. The average particle size was calculated to be  $18nm_{\pm}2nm$  and  $8nm_{\pm}2nm$ , as shown in histogram (c,f). SAED reveals the crystalline and semicrystalline nature of the nanoparticles (b,e). The XRD data is shown in Figure 2, (a) illustrates five unique reflection planes, all of which are allocated to 20 values according to JCPDS#87-641, 40° (111), 46.47° (200), 68.04° (220), 81.73° (311) and 86.23° (222). To study the effects of palladium nanoparticles on Fc and Fc-COOH redox electrochemistry, these two nanoparticles were used to form Fc-PdNP-1 and Fc-PdNP-2.



Figure 2. XRD pattern of the PdNP-1&PdNP-2

# **3.2. The Influence of Pd nanoparticle shape on Redox Electrochemistry of Ferrocene and Ferrocene carboxylic acid**

The role of EETMS, GPTMS, and 3-aminopropyltrimethoxysilane (3-APTMS) in the synthesis of gold nanoparticles (AuNPs) with regulated nano geometry has been thoroughly investigated [20]. A similar mechanism is found for the conversion of 3-APTMS capped Pd<sup>2+</sup> ions. The time taken to create noble metal nanoparticles ranges from 5 to 30 minutes, justifying the use of EETMS, 3-APTMS, GPTMS, formaldehyde, and PVP as the most efficient reagents. Here, we calcined the 3-APTMS stabilized nanoparticles at 500 °C after carefully adsorbing Pd nanoparticle-1 and Pd nanoparticle-2 on graphite powder. All organic components on Palladium nanoparticles were removed during calcination and subsequently used to understand their impact on the electrochemistry of Fc and Fcmc modified electrodes because the close interaction of PdNPs and Fc, Fc-COOH within graphite paste may facilitate the charge transfer rate during electrochemical measurements. On these topics, there have been some fascinating discoveries. The findings on the change in redox performance of Fc and Fc-COOH within the modified carbon paste electrode were examined first. The cyclic voltammograms of (a) CPE/Fc



(b) CPE/Fc-PdNP-1 (c) CPE/Fc-PdNP-2 (d)CPE/Fcmc (e)CPE/Fcmc-PdNP-1 (f) CPE/Fcmc-PdNP-2. electrodes at varied scan rates are shown in Figure 3.

**Figure 3.** Cyclic voltammetry of CPE/Fc (a), CPE/Fc-PdNP-1 (b), CPE/Fc-PdNP-2 (c), CPE/Fc-COOH (d), CPE/Fc-COOH-PdNP-1 (e), and CPE/Fc-COOH-PdNP-2 (f) in 0.1 M phosphate buffer (0.5 M KCl, supporting electrolyte) between 0 to 0.6 V vs Ag/AgCl at a range of scan rates starting at 0.01 Vs<sup>-1</sup>, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 Vs<sup>-1</sup> respectively

The drop in anodic ( $E_{pa}$ ) and cathodic ( $E_{pc}$ ) peak potentials is clearly justified, as illustrated in Figure 3. Furthermore, under comparable conditions, both anodic and cathodic peak currents steadily increase, showing a decrease in  $R_{ct}$  value as a function of palladium nano geometry, which is further validated by impedance spectroscopy. Following that, we used cyclic voltammetry and differential pulse voltammetry to investigate the dynamic electrochemistry in the presence and absence of varying concentrations of ascorbic acid, as ascorbic acid is an efficient electroactive species that can be used for both electrochemistry direct and mediated.

The results shown in Figure 4 convincingly support a notable increase in anodic current that is once again related to the electrochemical transformation of ascorbic acid, further demonstrating how palladium nanogeometry reduces charge transfer resistance.

An electroanalytical study of modified carbon paste electrodes was performed by amperometric measurement under stirring conditions.



**Figure 4.** Cyclic voltammograms at 10 mV/s in the absence (curve 1) and presence (curve 2) of ascorbic acid (5 mM) for CPE/Fc (a), CPE/Fc-PdNP-1 (b), CPE/Fc-PdNP-2 (c), CPE/Fc-COOH (d), CPE/Fc-COOH-PdNP-1 (e), and CPE/Fc-COOH-PdNP-2 electrodes

Figure 5 shows the results of amperometric measurements using AA (5  $\mu$ M to 1.6 mM) in a continuously stirred solution with an operating potential of 0.31 V vs Ag/AgCl. The CPE/Fc-COOH-PdNP-2 has higher responses than CPE/Fc-COOH-PdNP-1, CPE/Fc, CPE/Fc-PdNP-1and CPE/Fc-PdNP-2 modified electrode as illustrated in Figure 5, a standard curve for AA detection by amperometry was created. The findings point to a strong linear relationship between amperometric current and AA concentration.

The sensitivity of CPE/Fc, CPE/Fc-PdNP-1, CPE/Fc-PdNP-2, CPE/Fcmc, CPE/Fcmc-PdNP-1, and CPE/Fcmc-PdNP-2 electrodes for AA sensing changed into observed to be (11.03, 17.42, 23.36, 19.85, 33.02, and 43.96  $\mu$ A/mM), respectively, confirming the role of palladium and its nano geometry on electroanalysis and further confirmed via amperometric responses recorded at varying running potentials between 0.15 V and 0.4 V *vs* Ag/AgCl as proven in Figure 5.

Following that, the impact of palladium and its nanogeometry during electrochemical sensing was examined using differential pulse voltammetry (DPV) of CPE/Fc, CPE/Fc-PdNP-1, CPE/Fc-PdNP-2, CPE/Fcmc, CPE/Fcmc-PdNP-1, and CPE/Fcmc-PdNP-2 electrodes.

Figure 6 (a,b,c,d,e, and f) show differential pulse voltammograms at various ascorbic acid concentrations.



**Figure 5.** Amperometric response of (a) CPE/Fc (1), CPE/Fc-PdNP-1 (2), CPE/Fc-PdNP-2 (3), (b) CPE/Fc-COOH (1) CPE/Fc-COOH-PdNP-1 (2), and CPE/Fc-COOH-PdNP-2 (3) on the addition of varying concentrations of ascorbic acid, recorded at a constant potential of 0.31 V vs Ag/AgCl; (c) Calibration curve for ascorbic acid analysis using CPE/Fc (1), CPE/Fc-PdNP-1 (2), CPE/Fc-PdNP-2 (3), (d) CPE/Fc-COOH (1), CPE/Fc-COOH-PdNP-1 (2), and CPE/Fc-COOH-PdNP-2 (3), (e) system; Chronopotentiometry of CPE/Fc (1), CPE/Fc-PdNP-1 (2), CPE/Fc-PdNP-2 (3), (f) CPE/Fc-COOH (1) CPE/Fc-COOH-PdNP-1 (2), and CPE/Fc-COOH-PdNP-2 (3), (f) CPE/Fc-COOH (1) CPE/Fc-COOH-PdNP-1 (2), and CPE/Fc-COOH-PdNP-2 (3), (f) CPE/Fc-COOH (1) CPE/Fc-COOH-PdNP-1 (2), and CPE/Fc-COOH-PdNP-2 (3), recorded at a different operating potential between 0.15 to 0.4 V vs Ag/AgCl

Figure 7 shows the calibration curves for pulse voltammogram peak currents as a function of AA. With a progressive rise in Ascorbic acid sensitivity, a linear connection was found between differential pulse voltammetry current and AA concentration. The sensitivity of AA sensing for CPE/Fc, CPE/Fc-PdNP-1, Fc-PdNP-2, CPE/Fcmc, CPE/Fcmc-PdNP-1and CPE/Fcmc-PdNP-2 electrodes was found to be (7.45, 9.89, 12.18, 5.91, 12.31 and 16.75  $\mu$ A/mM), respectively, validating the role of palladium and its nanogeometry.

The findings in Figure 4 and Figure 6 can be investigated further to better understand the impact of palladium and its nanogeometry, as shown in Figure 8, which demonstrates the variation of the current function  $i_p / s^{1/2}$  as a function of scan rate.



**Figure 6.** Differential pulse voltammogram of CPE/Fc (a), CPE/Fc-PdNP-1 (b), CPE/Fc-PdNP-2 (c), CPE/Fc-COOH (d) CPE/Fc-COOH-PdNP-1 (e), and CPE/Fc-COOH-PdNP-2 (f) in the presence of varying concentrations of ascorbic acid ( $5 \mu$ M to  $1.6 \mu$ M)



**Figure 7.** (a) and (b) show the linear relation between differential pulse voltammogram peak currents *vs*. concentration of ascorbic acid

In the absence of AA, the results of the variation of current function on scan rate in all six cases CPE/Fc, CPE/Fc-PdNP-1, CPE/Fc-PdNP-2, CPE/Fcmc, CPE/Fcmc-PdNP-1, and CPE/Fcmc-PdNP-2 electrodes show a horizontal straight line, whereas, with ascorbic acid, the current function gradually decreases as scan rate increases and eventually tends to a straight line.

The characteristics of the proposed sensor are compared to those of existing sensors reported in the literature for the detection of ascorbic acid in Table 2.



**Figure 8.** The plot of current function vs square root of scan rate of CPE/Fc (a), CPE/Fc-Pd NP-1 (b), CPE/Fc-PdNP-2 (c), CPE/Fc-COOH (d) CPE/Fc-COOH-PdNP-1 (e), and CPE/Fc-COOH-PdNP-2 (f)

Table 2. Comparison of the CPE/Fc-PdNP-2 and CPE/Fcmc	-PdNP-2 with previously reported
sensors	

Electrode material	Method	<b>Detection limit</b>	Linear range	Reference
		(µM)	(µM)	
Pt foil	Amperometry	-	570-5680	[21]
ERGO <sup>a</sup> /GCE	DPV	250	500-2000	[22]
Pd-Pt/rGO	DPV	0.61	40-1200	[23]
MCM41	DPV	10	40-400	[9]
G <sup>b</sup> -30	SWV	17.8	5-1000	[24]
HNGA <sup>c</sup>	DPV	16.7	50-1500	[25]
7-hCNT/MA <sup>d</sup>	SWV	50	200-750	[26]
CuO/ rGO	CV	189	500-2000	[27]
PAni-TCNQ-Pd <sup>e</sup>	Amperometry	-	50-5000	[17]
CPE/Fc-PdNP-2	Amperometry	5	10-500	This work
CPE/Fcmc-PdNP-2	Amperometry	5	10-500	This work

<sup>a</sup> Electrochemically reduced graphene oxide.

<sup>c</sup> Holy nitrogen-doped graphene aerogel.

<sup>d</sup> Seven-hole carbon nanotube paste multielectrode array.

<sup>e</sup> Polyaniline tetracyanoquinodimethane Palladium.

<sup>&</sup>lt;sup>b</sup>G30-graphene ink.

In CPE/Fc-COOH-PdNP-2, the current function reaches a constant value at a faster scan rate than in CPE/Fc-COOH-PdNP-1, CPE/Fc-PdNP-1, CPE/Fc-PdNP-2, CPE/Fc-COOH, CPE/Fc, implying faster charge transfer dynamics as a function of palladium nanogeometry.

# 3.3. Study of Electrochemical Impedance Spectroscopy (EIS)

EIS experiments were also carried out to study the effect of change on charge transfer characteristics. Data was collected for CPE/Fc, CPE/Fc-PdNP-1, CPE/Fc-PdNP-2, CPE/Fcmc, CPE/Fcmc-PdNP-1, and CPE/Fcmc-PdNP-2 electrodes in 0.1M phosphates (with 0.5 M KCl) buffer between 1 Hz and 1000 kHz, and 0.31V potential were used as shown in Figure 9.



**Figure 9.** Nyquist plot of CPE/Fc (a), CPE/Fc-PdNP-1 (b), CPE/Fc-PdNP-2 (c), CPE/Fc-COOH (d) CPE/Fc-COOH-PdNP-1 (e), and CPE/Fc-COOH-PdNP-2 (f), (1) without adding AA, with AA- (2) 2.5 mM, (3) 5 mM and (4) 7.5 mM

Randle's circuit has two halves on a standard Nyquist plot: one is semi-circular, and the other is linear. At a lower frequency, the linear part corresponds to the mass transfer diffusion-restrained process, whereas, at a higher frequency, the diameter of the semicircle represents the charge transfer resistance. The charge transfer resistance ( $R_{ct}$ ) of the system is defined by the diameter of the circle component inside the Nyquist plot. CPE/Fc-COOH-PdNP-2 has a lower  $R_{ct}$  (1.58×10<sup>3</sup>) than CPE/Fc-PdNP-2 (1.96×10<sup>2</sup>), CPE/Fc-PdNP-1 (6.87×10<sup>3</sup>), CPE/Fc-COOH-

PdNP-1 (1.87×10<sup>3</sup>), CPE/Fc-COOH (8.3×10<sup>3</sup>), and CPE/Fc (12.8×10<sup>3</sup>), indicating that the system CPE/Fc-COOH-PdNP-2 has the highest charge transfer. In addition, as the concentration of ascorbic acid rises, the diameter of the circle shrinks, and the charge transfer process gradually accelerates. Table 3 shows the calculated charge transfer resistance values for CPE/Fc, CPE/Fc-PdNP-1, CPE/Fc-PdNP-2, CPE/Fcmc, CPE/Fcmc-PdNP-1, and CPE/Fcmc-PdNP-2 electrodes, demonstrating the impact of palladium and its nanostructures on the redox electrochemistry of Fcmc and Fc.

Modified Electrode	Fc	FcPdNP-1	FcPdNP-2	Fc-COOH	Fc-COOH- PdNP-1	Fc-COOH- PdNP-2
Concentration of ascorbic acid	R <sub>ct</sub>					
Blank	$60 \times 10^3$	$50 \times 10^3$	30×10 <sup>3</sup>	55×10 <sup>3</sup>	$45 \times 10^{3}$	$15.5 \times 10^{3}$
2.5 mM	$35 \times 10^{3}$	$19.5 \times 10^{3}$	5.39×10 <sup>3</sup>	$18.5 \times 10^{3}$	$4.76 \times 10^{3}$	$4.57 \times 10^{3}$
5 mM	$21.1 \times 10^{3}$	9.8×10 <sup>3</sup>	3.1×10 <sup>3</sup>	9.7×10 <sup>3</sup>	$2.34 \times 10^{3}$	$2.1 \times 10^{3}$
7.5 mM	12.8×10 <sup>3</sup>	6.87×10 <sup>3</sup>	1.96×10 <sup>3</sup>	8.3×10 <sup>3</sup>	$1.87 \times 10^{3}$	$1.58 \times 10^{3}$

**Table 3.** Proposed electrochemical sensor with Charge transfer resistance (R<sub>ct</sub>)

As a result, the charge transfer resistance of the Ferrocene and Ferrocene monocarboxylic acid modified electrode is reduced, allowing for faster dynamic electrochemistry.

### 4. CONCLUSION

The results of the experiments reveal that increasing the nanogeometry of Pd nanoparticles aids in improving the sluggish electrochemistry of Fc and Fc-COOH in Ascorbic acid sensing. This study aimed to accelerate the dynamic electrochemistry of Fc and Fc-COOH, which is significant with palladium's dual nanogeometry and its use in electrochemical sensing. As the nanogeometry of PdNPs changes, the electrochemistry of Fc and Fc-COOH improves. In the presence of palladium, the slow electrochemistry of the Fc and Fc-COOH modified electrode accelerates. An advantage of palladium and its nanogeometry in redox-mediated electrochemistry is still shown by the dependence of the current function on palladium nanostructures, even at higher scan rates. The detection limit for AA was 5  $\mu$ M, and the response for AA was linear between 10-500  $\mu$ M. These results show that the Fc-PdNP-2 and Fc-COOH-PdNP-2 exhibit excellent electrochemical sensing of AA by the modified electrode.

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# **Declarations of interest**

The authors declare no conflict of interest in this reported work.

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