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Development of a Sensitive Electrochemical Sensor for Tryptophan Detection with Ir-Pd/CNT Modified Electrodes

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ABSTRACT

In this study, a novel carbon nanotube-supported bimetallic Iridium-Palladium (Ir-Pd) catalyst, denoted as Ir(50%)-Pd(50%)/CNT, was successfully synthesized using the sodium borohydride reduction method for the electrochemical detection of L-Tryptophan (L-Trp). The catalyst was characterized using Elemental Dispersion X-ray (EDX-SEM) and X-ray Diffraction (XRD) techniques, confirming the effective dispersion of Ir and Pd nanoparticles on the carbon nanotube surface. Electrochemical performance was evaluated using Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV), and Electrochemical Impedance Spectroscopy (EIS) to optimize the sensor's detection capabilities. The resulting Ir-Pd/CNT/GCE sensor demonstrated a linear response over the concentration range of 100-1000 µM, and an exceptional limit of detection (LOD) of 0.02 µM at a signal-to-noise ratio (S/N) of 3. These findings indicate the potential of the Ir-Pd/CNT/GCE sensor for highly sensitive L-Trp detection in various applications, including biomedical, environmental, and food monitoring. This study emphasizes the promising role of bimetallic catalysts in enhancing the performance of electrochemical sensors for amino acid detection.

Keywords: Amino acid, Carbon nanotube, Tryptophan, Sensor.

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Introduction

L-Tryptophan (Trp) is an essential amino acid and is a precursor to the neurotransmitter serotonin [1]. Excessive levels of serotonin and melatonin have been shown to be associated with Alzheimer's and Parkinson's diseases. Therefore, it is necessary to develop a rapid and accurate method to determine Trp levels. Various techniques are currently used, including spectrofluorimetry [2], spectrophotometry [3], colorimetric [4], and electrochemical methods [5–8]. Electrochemical methods are preferred over others.There are many benefits to using electrochemical methods: the reaction rate can be controlled, measurements are usually specific to the oxidation or reduction step of an element, the method provides information about the activity of a chemical species, the equipment used in the method is less expensive than other methods, the reaction can be carried out under mild conditions, and the method is environmentally friendly [9].

Nowadays, the use of electrochemical sensors (Ecs) using modified electrodes is increasing, and a large amount of electrochemical research has been carried out using these sensors for the analysis of biologically active compounds [10]. Many investigations have been conducted on the electrochemical determination of Trp, and Table 1 lists the method, linear range, and limit of detection (LOD) values for each study. Based on research conducted on electrodes containing AgY/CPE [11], Nano-MIP/MWCNTs-GCE [12], Ce-ZnO/f-MWCNT/GCE [13], $ZnFe_2O4$NPs/CPE [14], and Ta_2O_5/RGO/GCE [15], it is seen that the linear range varies between 0.01 and 800 µM with good LOD values. Clearly, a large linear range and low LOD values are needed to develop and commercialize the Trp sensor.

Nanomaterials have a promising feature in improving the competitiveness of electrochemical sensors in amino acid detection. Because of their great mechanical stability, low cost, high surface area, high conductivity, and broad potential windows in aqueous systems, these nanomaterials are favored for the design of electrodes used in biosensors [19-20]. Carbon nanomaterials, such as graphene, carbon nanoparticles, carbon nanotubes, reduced graphene oxide (RGO), and carbon nanofibers (CNFs), are favored in this situation. Additionally, carbon nanostructure sensors have the advantages of lower detection limits, faster electron transfer kinetics, and higher sensitivity compared to other materials [21-22].

Table 1. Electrode materials used for L-tryptophan (Trp) electrochemical determination

Electrode	Method	Linear range	LOD/LOQ	Ref
AgY/CPE	DPV	0.01–1.2µM	0.0063/0.0189µM	[11]
MIP/MWCNTs-GCE	SDLSV	0.002–0.2µM 0.2- 10 µM 10 100µM-0.001µM	0.001/0.003µM	[12]
Ce-ZnO/f-MWCNT/GCE	DPV	0.01–0.1µM	0.0012µM	[13]
ZnFe2O4NPs/CPE	DPV	0.1–200.0µM	0.04µM	[14]
Ta2O5/RGO/GCE	SDLSV	1.0–8.0µM 8.0–80µM 80–800µM	0.84/2.52µM	[15]
Utg-C_3N_4 /GCE	LSV	110–0.1µM	0.024/0.72µM	[16]
Graphite electrode	DPV	5.0–150.0µM	1.73/5.19µM	[17]
Poly(L-Arg)/GCE	SWV	1.0–7.0µM	0.30/0.90µM	[18]
Ir-Pd/CNT/GCE	DPV	100-1000 µM	0.02-0.06µM	This study

In this study, the Ir-Pd/CNT catalyst was synthesized using the sodium borohydride reduction technique, a method known for producing well-dispersed and stable bimetallic catalysts. The electrochemical properties of the catalyst were assessed by modifying a Glassy Carbon Electrode (GCE) with the Ir-Pd/CNT composite. To evaluate the surface characteristics of the catalyst, Scanning Electron Microscopy with Energy Dispersive X-ray (SEM-EDX) and X-ray Diffraction (XRD) analyses were performed. These techniques provided insights into the morphology, elemental composition, and crystallinity of the catalyst, confirming its successful synthesis and dispersion on the carbon nanotubes.

The reason for selecting the Ir–Pd/CNT modified electrode for the determination of L-tryptophan is; the high electrochemical performance of the Ir–Pd/CNT-modified electrode in L-tryptophan detection is mainly due to the synergistic effect between Ir and Pd. When combined, these two metals improve electron transfer and create more active sites on the electrode surface. Ir provides strong oxidative ability and stability, while Pd helps in the adsorption and oxidation of nitrogen-containing molecules like tryptophan. This synergy lowers the energy required for oxidation and improves signal response. In addition, CNTs play a key role by offering a large surface area and excellent conductivity. They allow the Ir–Pd nanoparticles to disperse evenly and prevent aggregation, which increases the number of active sites available for reaction. The porous structure of CNTs also helps with fast electron movement and efficient contact between the analyte and the electrode. These combined properties explain the sensitivity, stability, and low detection limit observed in the sensor[23-25].

Compared with existing tryptophan sensors, the Ir–Pd/CNT sensor shows lower detection limits, wider linear range, and improved stability, highlighting its potential for practical applications.

Material and Methods

Materials

Sigma-Aldrich was the source of Ir ($IrCl_3.3H_2O$), and Pd ($PdCl_2$) 96%), sodium borohydride ($NaBH_4$, 99%), and multi-walled carbon nanotube (MWCNT, 98%), while Tryptophan (≥99.99%) was obtained from Carlroth. Nafion 117 solution (5%) was purchased from Aldrich and utilized. For electrochemical measurements, a three-electrode experimental system was used. The experimental setup was prepared as working electrode – glassy carbon electrode, reference electrode – Ag/AgCl, and counter electrode – platinum wire. Electrochemical measurements were taken using a Gamry Interface 1010 T potentiostat device. Deionized water was obtained through distillation utilizing a double distilled water purification system (Milli-Q Water Treatment System). All glass materials used in the study were washed with distilled water and ethyl alcohol, dried in an oven, and utilized.

The Synthesis of Ir-Pd/CNT Catalyst

The Ir-Zr/CNT-GCE catalyst was synthesized using the $NaBH_4$ reduction method with a 5 wt% Ir-Pd loading. Initially, distilled water, Ir precursor ($IrCl_3{\cdot}3H_2O$), and Pd precursor ($PdCl_2$) were combined in a beaker and mixed until homogeneously dispersed using an ultrasonic bath. Next, CNT support was added to the metal precursors dispersed in distilled water. The resulting mixture was sonicated and stirred magnetically for about 2 hours. Following this, sodium borohydride (30 equivalents) was introduced as a reducing agent, and the mixture was stirred for an additional hour. Finally, the obtained Ir–Pd/CNT catalyst was filtered after reduction, washed and dried at 85°C for approximately 12 h to obtain a powder mixture. Detailed procedure is given in the studies in the literature[26-28].

Electrochemical Studies

Electrochemical studies were performed on Ir-Pd/CNT with CV, DPV and EIS modified GCE electrodes using Gamry Interface 1010 T potentiostat in a three-electrode system. Glassy carbon (GCE) electrode was used as the working electrode, Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The nanocatalyst ink was obtained by uniformly dispersing 5 mg of nanocatalyst (Ir-Pd) into 1 mL of Nafion, and 3 µl of nanocatalyst ink was transferred to GCE and dried. For electrochemical research, an Ir-Pd/CNT modified GCE electrode was thus obtained. CV measurements were performed at room temperature in 0.1 M PBS + 5 mM L-Trp solution at pH 7.4 using the Ir-Pd/CNT modified electrode in the range (-0.8 V/0.6 V) (scan rate = 100 mV s^{-1}). Four different pH values were used to study the pH effect. Next, in a bimetallic Ir-Pd/CNT modified GCE electrode, the impact of concentration on the electro-oxidation of L-Trp was examined. The scan rate for L-Trp electrooxidation was determined by measuring various scan intervals. Lastly, CV measurements were carried out for a number of tried tests, such as L-tryptophan, glucose, uric acid, and ascorbic acid.

Results and Discussion

Physical Characterization

SEM-EDX and mapping analyses were performed to thoroughly examine the surface structure and elemental composition of the catalyst. The SEM images, shown in Figure 1, revealed the successful formation of carbon nanotube (CNT) structures, alongside the presence of metal nanoparticles, which are critical components for the catalytic activity. The catalyst of interest, Ir-Pd/CNT, was specifically analyzed within the region highlighted in Figures 1a and 1d to study the distribution of the components at a microscopic level.The results from the EDX analysis indicated that the region contained carbon (C), iridium (Ir), and palladium (Pd), which are the key elements in the catalyst. These findings were consistent with the intended design of the catalyst, confirming that both metal nanoparticles (Ir and Pd) were successfully incorporated onto the CNT structures. The EDX spectra, shown in Figure 1f, provide the weight percentages and atomic ratios of Ir and Pd, offering a quantitative understanding of the elemental composition of the catalyst. These values are essential for evaluating the effectiveness of the catalyst in terms of its metal loading and the potential impact on catalytic performance.The mapping analysis, combined with the SEM-EDX results, further supports the conclusion that the desired catalyst structure has been achieved. The homogenous distribution of Ir and Pd on the CNT surfaces, as indicated by the mapping, suggests that the catalyst has been effectively synthesized, ensuring that both metals are present in the required amounts and configuration for optimal catalytic activity.

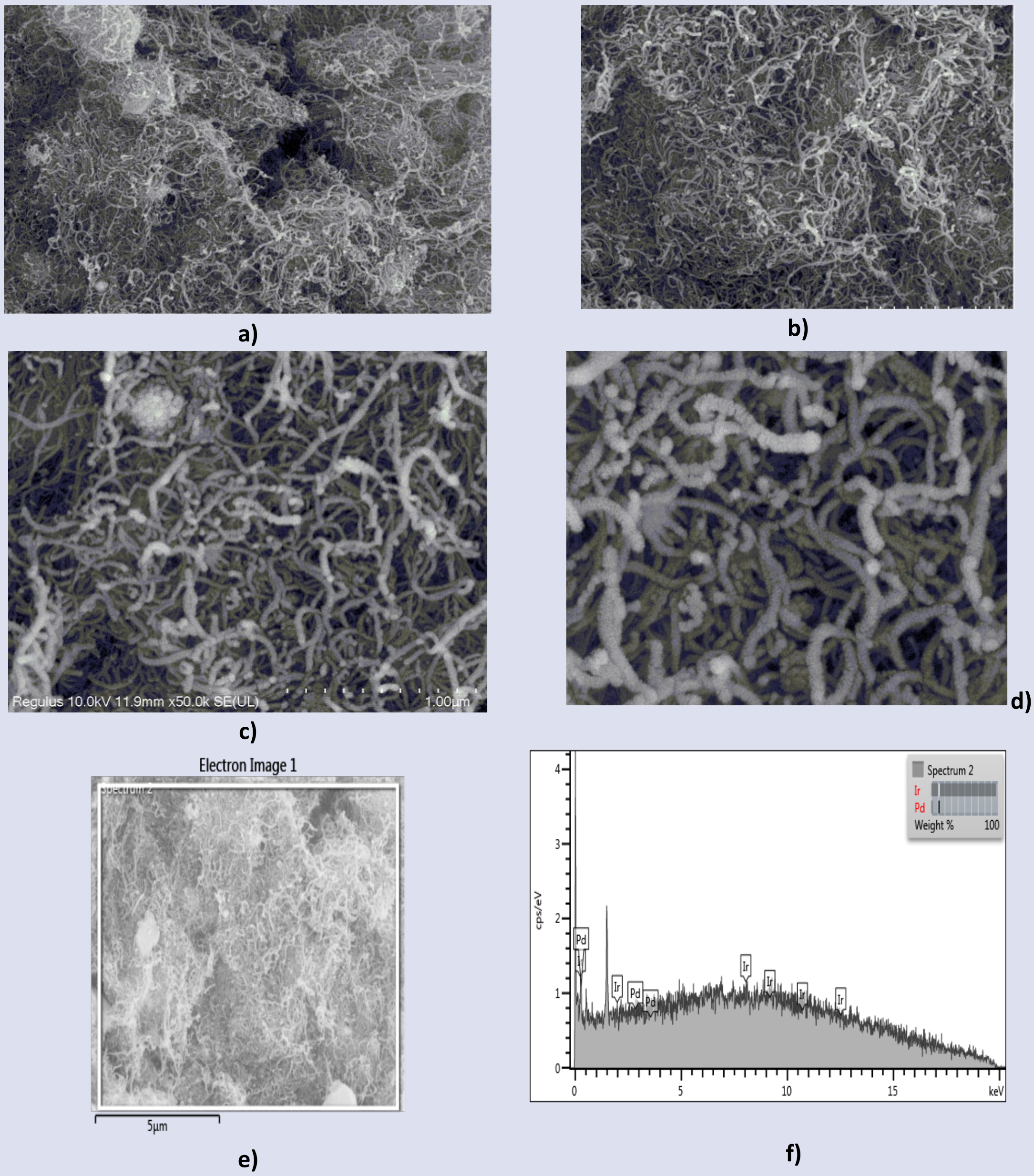


Figure 1. SEM-EDX and mapping of Ir-Pd/CNT catalyst.

The carbon peak in the (0 0 2) plane of the carbon nanotube was observed at 2Ɵ = 25.60 (Figure 2). In addition, the peak observed at 43.5° is indexed to the C (100) crystal plane. Other broad peaks at 40.8° (111), 47.4° (200), 69.3° (220), 83.6° (311), and 88° (222) were found to be typical Ir peaks [29]. Also (1 1 1), (2 0 0), (2 2 0) and (3 1 1) are prominent peaks for Pd [30].

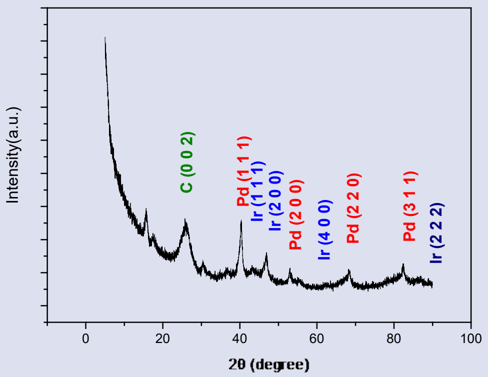


Figure 2. XRD pattern of 5% Ir-Pd/CNT catalyst

Electrochemical Measurements

A GCE for L-Trp measurement was modified using the modified Ir-Pd/CNT catalyst system. The electrooxidation capabilities of L-Trp amino acid was investigated at four distinct pH levels using a modified GCE electrode in 0.1 M PBS. The pH of 7.4 produced the best current (Figure 3).

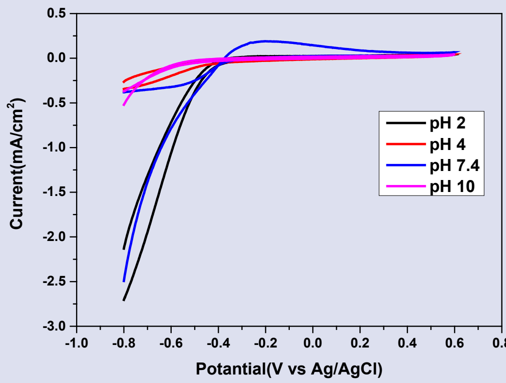


Fig. 3. Measurements of cyclic voltage were performed on an Ir-Pd/CNT modified GCE electrode in 0.1 M PBS + 5 mM L-Trp at a scan rate of 100 mV/s, and at pH values of 2, 4, 7.4, and 10.

Utilizing an Ir-Pd/CNT modified GCE electrode, the influence of L-Trp concentration on electrooxidation activity was examined. The current density of L-Trp electrooxidation was measured at four different concentrations (0, 5, 10, and 20 mM), and the results are shown in Figure 4. The results show that there is a direct relationship between the L-Trp concentration and the current density values for L-Trp electrooxidation.

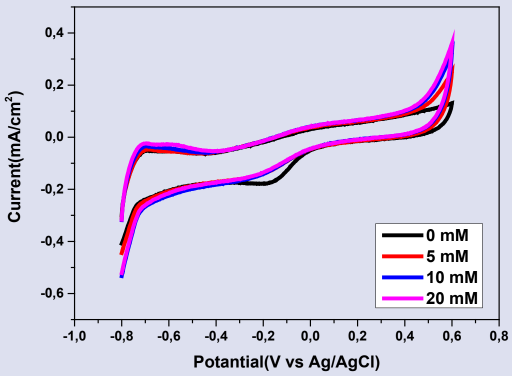


Figure 4. CV analyses of 4 different concentrations of Ir-Pd/CNT catalyst.

The scan rate on an Ir-Pd/CNT modified GCE electrode was measured using CV. The data in Figure 5 demonstrate that there is a direct correlation between the scan rate and the electrochemical oxidation current of L-Trp. This result is verified by the occurrence of controlled diffusion.

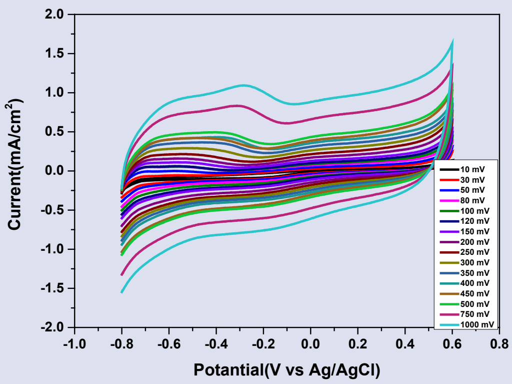
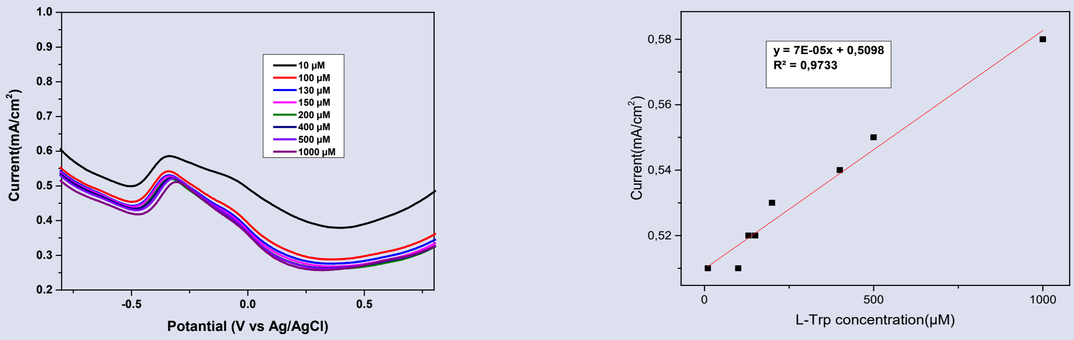


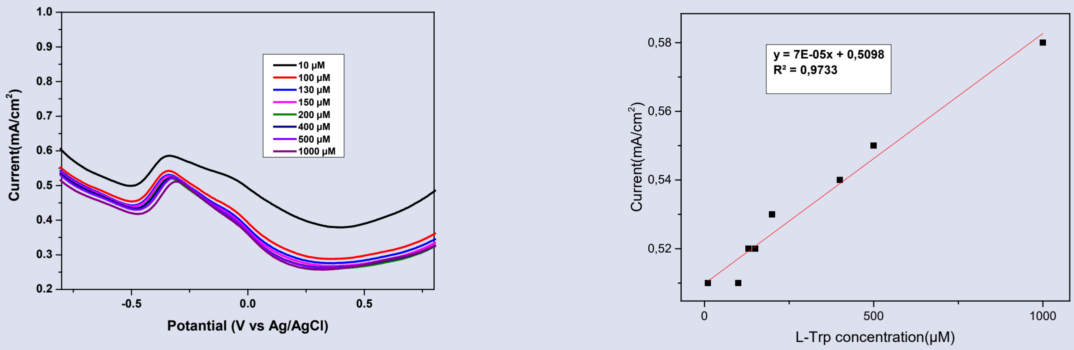
Figure 5. Cyclic Voltammograms on Ir-Pd/CNT modified GCE electrode in 0.1 M PBS (pH=7.4) + 5 mM L-Trp solution at different scan rates (10-1000 mV/s).

The DPV method was used to assess the L-Trp detection technology research. Plotted maximum intensity current values resulting from the concentration curves are displayed in Figure 6a. The L-Trp sensor based on Ir-Pd/CNT showed an intermittent response, with a current sensitivity of 7E-0,6mA/mM, a limit of detection (LOD) of 0.02 µM ,and a limit of quantification of 0.06 µM at S/N = 3. (Figure 6b). These findings show that the method is sensitive to L-Trp and can identify it at low concentrations.



a) b)

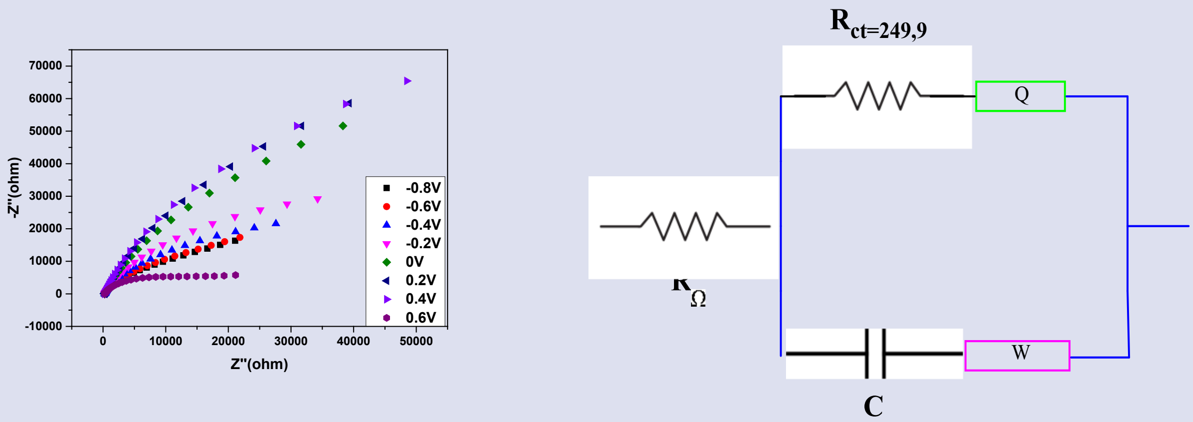
Figure 5. Cyclic Voltammograms on Ir-Pd/CNT modified GCE electrode in 0.1 M PBS (pH=7.4) + 5 mM L-Trp solution at different scan rates (10-1000 mV/s).



a) b)

Figure 6. a) DPV measurements on Ir-Pd/CNT modified GCE electrode in 0.1 M PBS (pH=7.4) + 10 µM-1000 µM L-trp solution, b) Linear regression of maximum current versus L-Trp concentration.

The EIS technique is utilized to evaluate electrode capacitance, measure charge transfer resistance, and explore diffusion behaviors simultaneously. The Nyquist plot generated from EIS data consists of a semicircular portion representing charge transfer and a linear segment corresponding to the diffusion-controlled process. As illustrated in Figure 7, the Ir-Pd/CNT-modified GCE electrode in a 0.1 M PBS and 5 mM L-Trp solution shows the lowest charge transfer resistance at 0.6 V, indicating its optimal electrochemical performance.



a)

b)

Figure 7. Electrochemical impedance spectrum at different potentials of Ir-Pd/CNT modified GCE electrode at 0.1 M PBS (pH 7.4) + 5 mM L-trp, b) R_{ct} value

The interference study was conducted to evaluate the ability of the sensor to distinguish L-Trp from other common organic compounds present in the blood buffer medium, considering the specific characteristics and sensitivity of the sensor. The aim was to determine the selectivity of the sensor towards L-Trp, which is crucial for accurate detection in complex biological samples. The findings revealed that L-Trp was significantly more distinguishable compared to other substances such as D-Glucose, uric acid, L-Tyrosine, and ascorbic acid. These results indicate that the sensor effectively minimizes interference from these commonly found compounds, as shown in Figure 8a-b, which highlights the clear separation and distinct signals for L-Trp in the presence of these potential interfering substances.

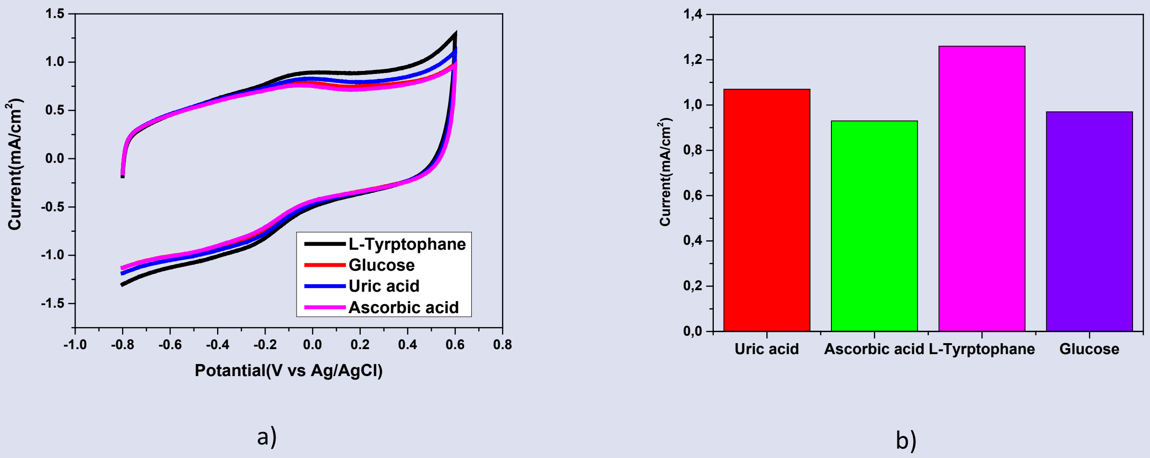


Figure 8. a)0.1M PBS (pH 7.4)+ 5 mM L-Trp for sensivity to L-Trp interferances CV at 100 mV/s, b) interference resistance diagram

Conclusions

In conclusion, the Ir–Pd/CNT catalyst has shown outstanding performance in the electrochemical detection of L-tryptophan (L-Trp), a biomolecule of critical relevance in medicine, food quality control, and environmental analysis. The catalyst was synthesized via sodium borohydride reduction, yielding a well-dispersed bimetallic nanostructure anchored on carbon nanotubes. This structure was confirmed through SEM-EDX and XRD analyses, which revealed uniform particle distribution and clear crystallinity. Electrochemical studies using CV, DPV, and EIS demonstrated that the Ir–Pd/CNT-modified electrode exhibited high sensitivity, low detection limits, and efficient electron transfer kinetics. The sensor maintained a wide linear detection range and demonstrated notable long-term stability, making it a reliable platform for real-world applications. Given its performance, the sensor holds promise for use in biomedical diagnostics, environmental monitoring, and the food industry—especially in detecting trace amounts of L-Trp and monitoring amino acid content in complex samples. Future research may focus on enhancing the selectivity of the sensor in complex biological or environmental matrices, and on adapting this platform for the detection of other clinically or industrially relevant biomolecules. Overall, this work contributes to the development of cost-effective and high-performance electrochemical sensors based on non-enzymatic, noble-metal-supported nanomaterials.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could influence the work reported in this paper.

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