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## **Curcumin Nanoparticle/AgNPs/Multiwalled Carbon Nanotube Nanocomposite as a Novel Electrochemical Sensor for Electrocatalytic Simultaneous Determination of Adrenaline and Tryptophan**

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A novel highly sensitive and selective electrochemical sensor with a low limit of detection and wide linear ranges for electrooxidation of adrenaline (Adr) and tryptophan (Trp) were utilized by immobilization of curcumin nanoparticles, AgNPs on MWCNTs on the glassy carbon electrode. The SEM and XRD analyses were applied for the characterization of the fabricated sensor surface. The diameter of synthesized nanoparticles was obtained at 39 to 64 nanometers using SEM analysis. The CV peak currents of Adr and Trp were linear in the range 1.0-1150  $\mu\text{M}$  and 0.5-1200  $\mu\text{M}$ , respectively. The detection limit was found 0.058  $\mu\text{M}$  and 0.032  $\mu\text{M}$ , for Adr and Trp, respectively. The fabricated nanocomposite was successfully employed to determine Adr in an adrenaline injection solution as well as Adr and Trp in a human urine sample. The calculated recovery values confirmed that electrochemical was appropriate for the precise and accurate simultaneous determination of target Adr and Trp in complex mixtures with recovery in the range of 98-103%.

**Keywords:** Electrochemical sensor, Adrenaline, Tryptophan, Curcumin nanoparticles, MWCNTs

### **INTRODUCTION**

Adrenaline (Adr), a neurotransmitter found in natural body fluids, plays a critical part in the central nervous systems, renal, hormonal, and cardiovascular systems' functions [1,2]. Adr affects physiological functions such as heart rate and blood pressure and aids in stress and quick action reactions [3,4]. Shakiness, nervousness, and perspiration are all side effects of too much adrenaline. Because too much adrenaline in the body affects blood pressure, heart rate, and the immune system, people with Parkinson's disease have low levels of it. As a result, quantifying Adr in various human fluids is an important approach for learning about nerve physiology, making diagnoses, and managing medications [1].

Tryptophan(2-amino-3-(1H-indol-3-yl)-propionic acid), is an essential amino acid in the human body that plays a key

role in a variety of metabolic processes, including protein structure [5], brain functioning [6], and creating and maintaining a positive nitrogen balance [7]. Trp is also a precursor to the neurotransmitter serotonin.

Several spectroscopic, chromatographic, and electrophoresis techniques have been developed for the determination of Adr and Trp [8-14]. Considerable attention has been paid to the determination of targets by electrochemical techniques. These methods have the advantageous of simplicity, sensitivity, and accuracy [15, 16].

In the fields of biochemistry, neurochemistry, and medicine, the simultaneous measurement of Adr and Trp is critical [17,18]. However, determining species using standard bare electrodes is quite challenging. In real biological samples, Adr and Trp generally coexist, and the results suggest that the sprinkling of Adr has an effect on human plasma tryptophan [1]. Furthermore, the research indicates that the direct oxidation of Adr and Try at the bare electrode

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required significant overpotentials and that their oxidation potentials are frequently quite close to each other, with their signals overlapping. Hence, they may interfere with each other determinations [2,15]. For these reasons, modification of the electrode surface is necessary for analytical application and diagnostic research.

Our literature survey reveals that modified glassy carbon and carbon paste electrodes have been designed and fabricated to solve the above problems. Nanostructured materials particularly different types of carbon-based nanomaterials have been considered due to their excellent physical, chemical, interesting electrical, mechanical, and catalytic properties [1,15,19,20]. Also, graphene-supported metal NPs and metal oxide nanoparticles grafted graphene have been proposed for the determination of targets using various methods [3,20].

Transitional metals such as Cu and Ag nanoparticles (NP) can further improve the charge and mass transfer of the carbon-based nanoparticles and result in better sensitivity by increasing surface area [15,20]. Also, nanocomposites of carbon-based nanoparticles and metal oxides show different physical, electrical, optical, mechanical, and thermal properties that enable their applicability in catalytic and electrochemical technologies [3,21,22].

In recent years, particular attention has been paid to using silver nanoparticles (AgNPs) in various research areas. AgNPs have been synthesized using a variety of chemical and physical procedures. Many of these synthetic methods apply toxic chemicals (reducing agents) or capping agents and these chemicals are hazardous to environmental and biological systems [15]. Hence, the development of efficient and environmentally friendly methods is always considered. Green synthesis of AgNPs has been considered as a simple, appropriate, and alternative with respect to the chemical methods. Different plant species or their extracts have been applied for this purpose [23,24]. The polysaccharides, proteins, and some secondary metabolites act as reducing and stabilizing agents in these syntheses [25,26].

Curcumin, also known as 1,7-bis-(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, is a hydrophobic chemical found in turmeric [27]. Different analytical, and clinical studies reveal that curcumin (CMNPs) has antimicrobial, anti-inflammatory, anticancer, antioxidant, and other therapeutic activities [15]. Curcumin does not have

a high bioavailability. Conjugation of curcumin on metal nanoparticle surfaces is one of the possible ways to increase curcumin bioavailability.

It has been found, for example, that CM can bind to the surface of gold nanoparticles [15,28]. Also, we previously, showed that CM stabilized and functionalized AgNPs decorated SDS/MWCNTs glassy carbon electrode [15].

Many studies have also shown that adrenaline secretion affects plasma-free tryptophan levels [29,30]. Adr has a great influence on the functioning of biological systems in the human body. Tryptophan and adrenaline are present in biological samples. So, the determination of these species is very important. In the present study, a very sensitive and selective electrochemical method was proposed for this purpose. Therefore, CMNPs were bonded on the surface of GCE modified with AgNPs and MWCNTs (CMNPs/AgNPs/MWCNTs/GCE), and a new sensor was developed for the simultaneous determination of Trp and Adr. The constructed nanocomposite demonstrated a high catalytic activity for targets. In comparison to the bare GCE and MWCNTs/GCE electrodes, results showed that the analytes' oxidation peak potential shifted to less positive values. Also, the response of the modified electrode was not significantly affected by common interferences such as metal ions, anions, and other biomolecules. Our findings indicate the excellent limit of detection for Adr with respect to other published works.

## EXPERIMENTAL

### Materials and Methods

Silver nitrate, tryptophan, adrenaline, multi-walled carbon nanotube (MWCNT) (more than 95% purity), sodium hydrogen phosphate, disodium hydrogen phosphate, sodium hydroxide, potassium chloride, phosphoric acid, hydrochloric acid, and acetic acid were purchased from Merck and Aldrich with analytical grade. The materials were used without being purified further. The studies were conducted with doubly distilled water. Adrenaline and tryptophan stock solutions were made at a concentration of  $5.0 \times 10^{-3}$  M.

Daily, an adrenaline solution was made with a very small quantity of sodium hydroxide. An injection solution of Adr was obtained from a local pharmacy. Curcumin longa powder

(0.15 g) was extracted in 5 ml ethanol at 50 °C using sonication (400 W, 50 kHz). The yellow supernatants were collected and kept at 4 °C for future use.

### Apparatus

The three-electrode setup was constructed utilizing CMNPs/AgNPs/MWCNT/GCE as the working electrode; and Ag/AgCl and platinum wire as reference and counter electrodes, respectively. A Swiss Metrohm type 713 pH/mV meter was used to take the pH measurements. XRD, FTIR, UV-visible, scanning electron microscopy (SEM-EDX, XL30, Philips Netherland), and electron microscopy (TEM) with a Zeiss-EM10C at an accelerating voltage of 80 kV were used to characterize the nanocomposite thoroughly.

### Preparation of Alga Extract

Sargassum, a brown alga, was obtained off the coast of Bushehr, Iran, on the Persian Gulf. In a plastic bag, the gathered algae were quickly carried to the laboratory. To remove interfering materials, the algae samples were washed many times in both tap and distilled water. They were dried in the shade for a week to eliminate any moisture. The powder then was dried in the oven (at 60 degrees Celsius) and ground with an electric mixer. After that, a weighted amount (2.0 g) of dry marine alga powder was dissolved in 20 ml of distilled water and heated for 20 min at 60 °C. The solution was then filtered using a Whatman no. 1 vacuum filter pump. [31]

### Biosynthesis of AgNPs by Algal Powder

2.0 g of silver nitrate was added to 20 ml of the algal extract in a 100 ml conical flask. To ensure that the metal ion reduction was complete, the flask was gradually and indirectly heated to 60 °C and agitated for 48 h using a magnetic stirrer [26]. AgNPs are formed when the color of the solution changes from yellow to brown.

### Synthesis of CMNPs

Extraction of CM was performed using of ultrasonic power of 300 W and 70 °C for 25 min. For extraction 5 ml ethanol was added on 0.15 g of turmeric powder. After extraction, the yellow supernatants were collected and stored at 4 °C until needed. The yellow supernatants were collected after extraction and kept at 4 °C until they were needed.

### Fabrication of Nanocomposite (CMNPs/AgNPs/MWCNT/GCE)

The graphitic nanoparticles, amorphous carbon, and other residues were removed by heating 0.50 mg MWCNTs in a nitrogen environment for 2 h in a 400 °C oven. MWCNTs were then dispersed in 50 ml of 6.0 M HCl for 4 h under ultrasonic agitation in a nitrogen atmosphere. the solution was then filtered using a Whatman 42 filter paper and washed with distilled water until it reached a pH of 7.

In an adequate amount of dichloromethane, the treated MWCNT (10% w/w) was combined with fine graphite powder. AgNPs, 30 µl, and 40 µl CMNPs solution were mixed with 10% w/w MWCNT. After the dichloromethane had completely evaporated, the composite was air-dried for 24 h [31].

## RESULTS AND DISCUSSION

In this study, the fabrication of a highly sensitive and selective electrochemical sensor for the simultaneous determination of Trp and Adr is desired. It is very difficult to detect and measure targets by direct electrochemical detection with conventional electrodes. Determining them by unmodified electrodes requires high overvoltage to perform oxidation or reduction reactions. They are also oxidized on the surface of solid electrodes at potentials close to each other. The oxidation peaks of analytes at the GE bare electrode are given in Fig. 3. The scale of the Try and Adr cyclic voltammogram was changed in the secondary axis for clarity in Fig. 3a and 3b, respectively. According to Fig. 3, Adr shows a broad anodic peak at a range of 0.71 to 0.91 V, and Try anodic peak was shown at 1.1 V. Therefore, their voltammetric responses will overlap.

The electrochemical response of tryptophan at the modified electrode surface that was observed at 0.34 V most likely represents the oxidation of tryptophan to its oxidized derivatives. The indole ring on tryptophan can be oxidized, resulting in the creation of several oxidation products such as indole-3-pyrrole carboxylic acid or other indole derivatives. Adrenaline is oxidized to produce oxidized forms like adrenalinequinone or adrenochrome, as seen by the peak at 0.021 V. The particular oxidation potentials are dependent on the electrode surface, pH, and experimental setup. The peak at 0.02 V, which shows the electrochemical reaction of

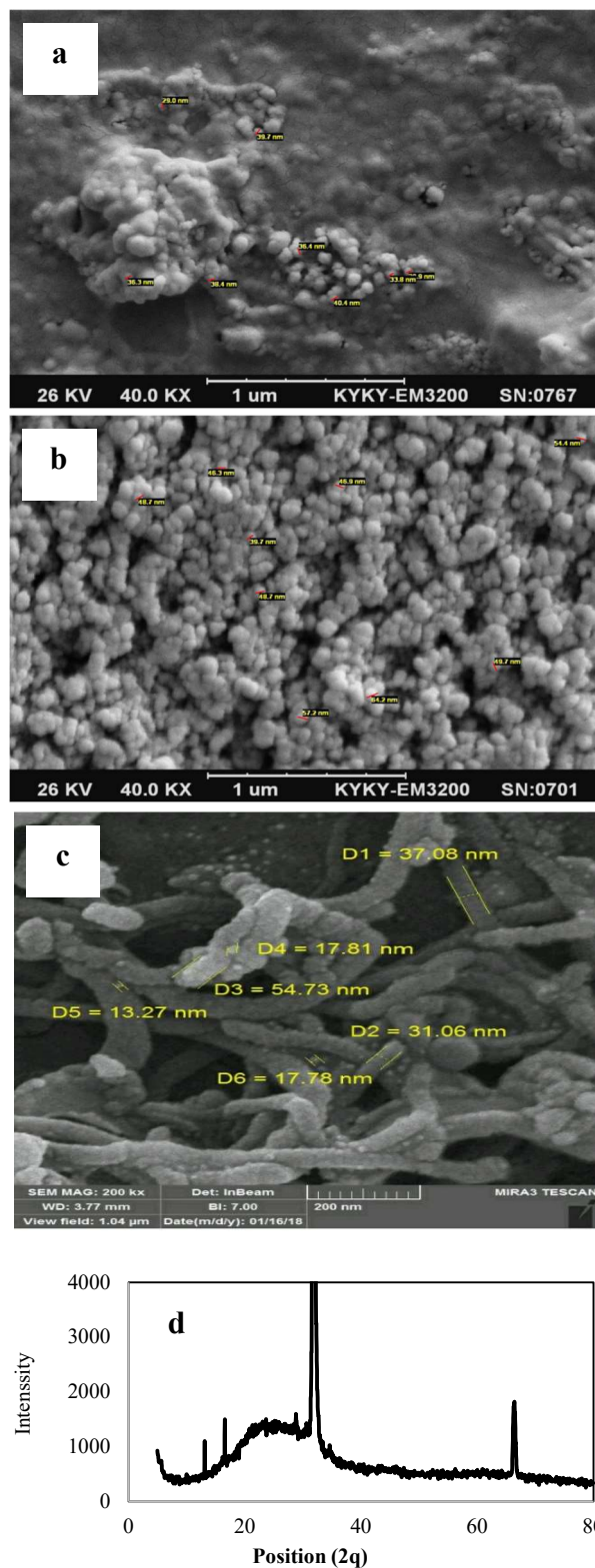
adrenaline at the altered electrode surface, denotes the beginning of this oxidation process.

Also, this figure depicted that Trp and Adr show much smaller anodic peak response at bare GC electrode. Whereas using a modified electrode, Trp exhibits a sharp and strong oxidation peak at 0.860 V and Adr at 0.421 V with greatly increased peak current response, which approximately is a 7-fold increase in comparison with that at the bare GCE. Hence, to overcome the mentioned problem and increase the sensitivity of determinations, silver nanoparticles, curcumin nanoparticles, and MWCNTs were immobilized on the MWCNTs/GCE electrode (CMNPS/Ag/MWCNTs/GCE). With this modification, a very selective and sensitive method was developed for the simultaneous determination of analytes in drug and urine compounds. The effect of pH, scan rate, and amounts of modifiers on the peak current and peak potential has been investigated. In this section, we will discuss the fabrication of nanocomposite and the optimization of instrumental and laboratory conditions for measuring these two species.

### Characterization of Fabricated Nanocomposite

Curcumin was extracted from turmeric longa powder, which is widely available on the market as an herbal drug at a cheaper cost than pure curcumin. The synthesized CMNPs have a size range of 33-74 nm, according to the SEM image (Fig. 1a). Figure 1b shows the SEM image of AgNPs. AgNPs produced a spherical structure with a wide range of diameters and heterogeneous dispersion, as shown in this diagram. The diameter of nanoparticles ranged from 39 to 64 nanometers. The image of the nanocomposite in Figure 1c indicates that CMNPs/AgNPs are well dispersed across the MWCNT/GCE surface. Also, this diagram depicts the random distribution of modifiers on the electrode surface, which could result in high loading and rapid analyte response.

Figure 1d also shows the XRD patterns of composite structures. Curcumin showed characteristics at 13.1° and 17.1° in this diagram. the characteristic peak at 28.8° contributed to MWCNT, and AgNPs in peaks at 33.5°, and 66.35° belongs to AgNPs. Hence, as a result of the XRD data, the composites are made up of CMNPs, AgNPs, and MWCNTs.



**Fig. 1.** SEM image of (a) CMNPs, (b) AgNPs and (c) CMNPs/AgNPs/MWCNTs, (d) XRD image of CMNPs/AgNPs/MWCNTs.

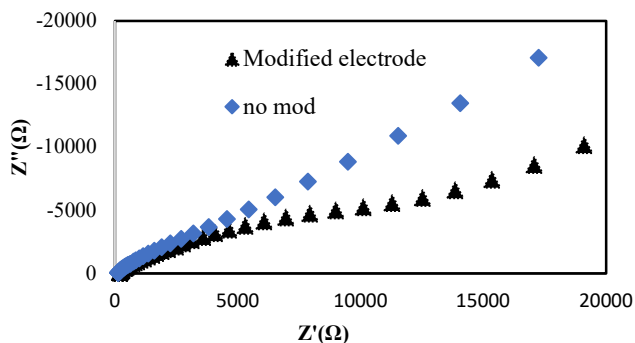
### Electrochemistry Characteristic of the Modified Electrode

EIS (electrochemical impedance spectroscopy) reveals the features of the electrode-electrolyte interface. The characteristics of GCE and CMNPs/AgNPs/MWCNT interfaces were compared using this approach. Figure 2 shows the Nyquist plots for both the bare and modified electrodes.

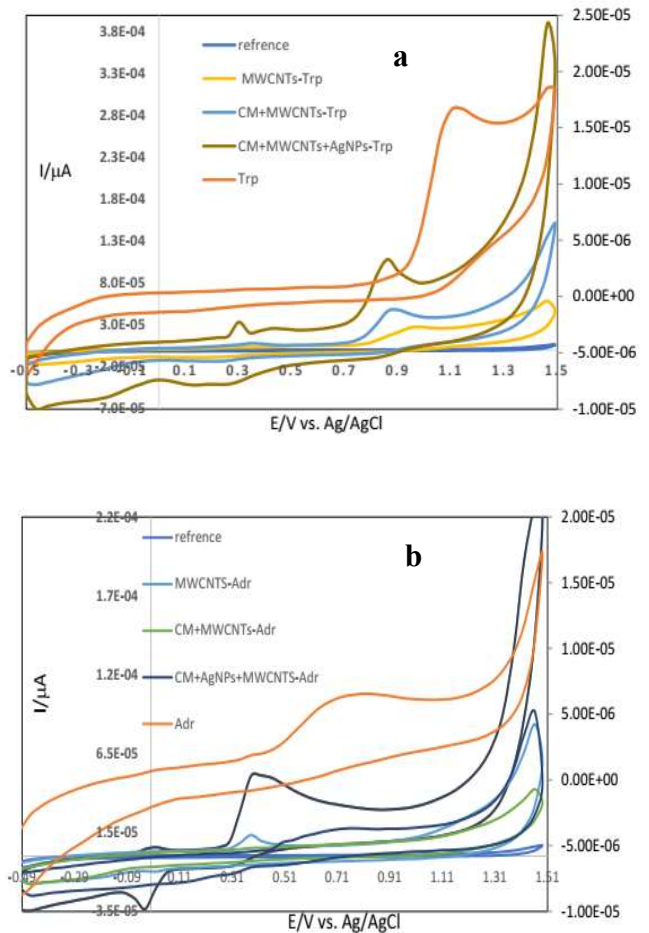
The EIS data of electrodes were collected in the ac frequency range of 5 Hz-10 kHz, with a wave amplitude of 5 mV and an oxidation potential of 0.86 V, which corresponded to Trp anodic peak potential ( $E_{pa}$ ).

As the diagram shows, the resistance of the modified electrode to electron transfer is less than that of the bare electrode. As a result, the manufactured nanocomposite (CMNPs-AgNPs/MWCNT) has better conductivity than the unmodified GCE electrode. So, MWCNTs and CMNPs on the GCE electrode improved electron transfer kinetics since charge transfer resistance ( $R_{ct}$ ) values are directly associated with electron transfer kinetics at the electrode/electrolyte interface. Hence, the fabricated nanocomposite was applied for construction of an electrochemical sensor.

At pH 3, cyclic voltammetry was applied to understand the electrochemical behaviors of the modified electrode surface. The electrochemical characteristics of Trp and Adr ( $2.0 \times 10^{-4}$  M) were examined. Trp has an oxidation peak at 0.51 V in bare GCE. Figure 3 shows the CV voltammograms of various electrodes GCE, MWCNTs/GCE, CMNPs/MWCNTs/GCE, and CMNPs/AgNPs/MWCNT/GCE at pH=3 and scan rate 50 for (a) Trp and (b) Adr.



**Fig. 2.** Nyquist plots of  $5 \times 10^{-4}$  M Trp in 0.1 M phosphate buffer of pH 3.0 containing 1.0 M  $KNO_3$  using different electrodes at the oxidation peak potential of Trp; (■) for bare electrode and (▲) for modified electrode.



**Fig. 3.** CV values of different electrodes GCE, MWCNT/GCE, CMNPs/MWCNTs/GCE, and CMNPs/AgNPs/ MWCNT/GCE at pH=3 and scan rate 50 for (a) Trp and (b) Adr.

The peak current was increased by 2, 5, and 16 times for Trp and for 1.5, 4, and 7 times for Adr, higher than bare GCE. Also, the voltammograms shifted to the less positive potentials. This confirms that catalytic oxidation of Trp and Adr was accomplished on the surface of the modified electrode. This is due to MWCNTs existence of sidewall defect sites, which operate as an electroactive site for analyte oxidation by enhancing the electron transfer rate. As a result, an increase in surface area correlates to an increase in current. This is due to the high surface area of CMNPs and AgNPs, which leads to an increase in Trp and Adr oxidation current [15].

### Investigation of Experimental Condition

**Influence of pH.** Figure 4 shows the voltammograms of species, recorded in the pH range of 3.0 to 8.0. The position of oxidation peaks and the intensities of peaks have varied by changing pHs, however the overall shape of the CV curves remained constant. Trp has an amino group with  $pK_a$  9.39 and a carboxylic acid with  $pK_a$  2.38. As a result, electrochemical oxidation of analytes is involved in the proton transfer process (Fig. 1S). In other words, pH affects the protonation states of the analytes, which in turn affects the CMNPs/AgNPs/MWCNT/GCE reaction to Trp. Trp showed the largest oxidation current peak at pH 3.

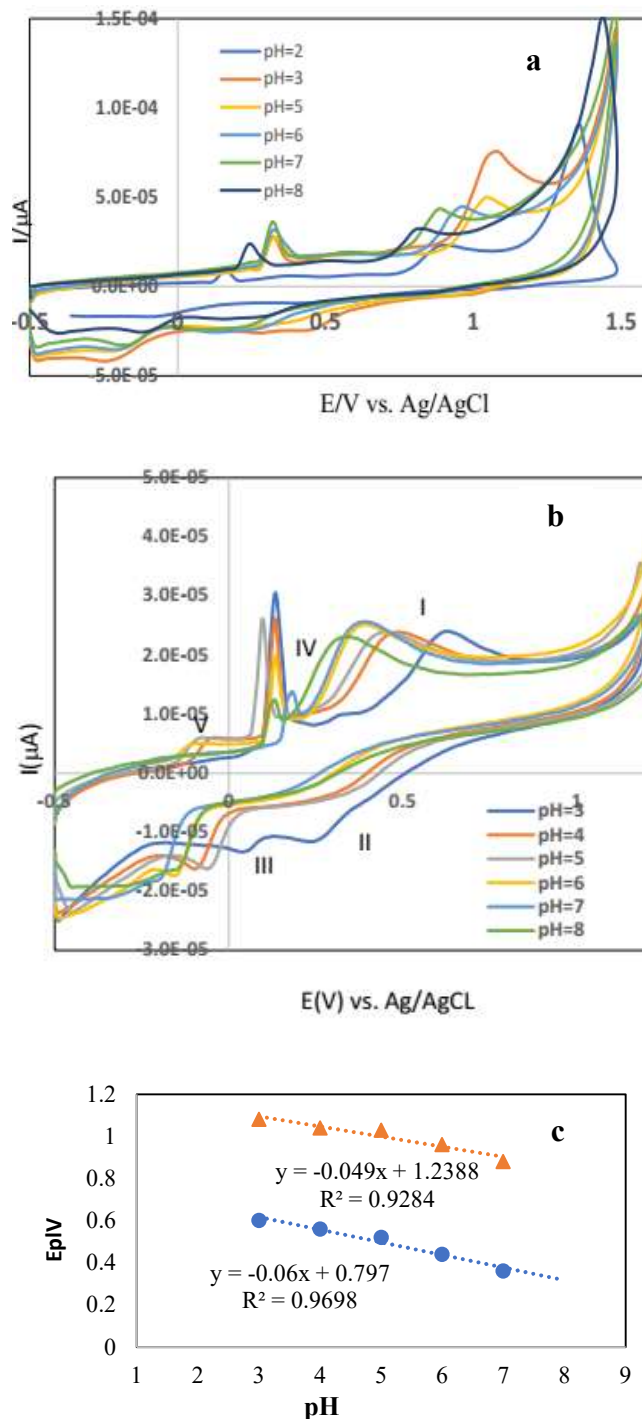
Also, Fig. 4b shows the oxidation potentials of Adr. According to this figure, two oxidation peaks of +0.321 V and +0.544 V were observed on the anodic scan of the CM/AgNPs/MWCNT/GCE electrode, in the pH range of 3-7 (Fig. 4b). These results suggested that acidic conditions were better for sensitive Trp and Adr detection.

As shown in Fig. 1S, to create adrenalinquinone, the neurotransmitter (Adr) undergoes a quasi-reversible two-electron oxidation with two protons [32]. At above pH 3 the cyclization reaction of Adr is possible (See Fig. 1S). Peak I, oxidation of adrenaline (Reaction 1); Peak II, reduction of adrenalinequinone (reaction 2); Peak III, reduction of adrenochrome (reaction 3); Peak VI, oxidation of leucoadrenochrome (reaction 4).

Over the entire pH range, the relationship between peak potential and pH is linear (4c and d). The regression equation was obtained  $E(V) = 0.049 \text{ pH} + 1.24$  and  $E(V) = 0.06 \text{ pH} + 0.0797$  for Trp and Adr, respectively.

At 25 °C, the slope of linear graphs was close to the Nernstian theoretical value of 0.059 V. This model assumes that the number of protons in electrochemical processes is equal to the number of transferred electrons. The electrochemical oxidation of Adr and Trp followed the loss of  $2e^-$ , according to the findings (see Fig.1S and 2). As a result, pH 3 is the best pH for determining Adr and Trp at the same time.

**Scan rate effect.** The relationship between peak current and scan rate can provide useful information about the electrode reaction mechanism (rate-determining step). Hence, using constructed nanocomposite in the range of  $10\text{-}100 \text{ mV s}^{-1}$ , the influence of scan rate on the oxidation peak current of Adr and Trp was investigated.



**Fig. 4.** Cyclic voltammograms of (a) Trp, (b) Adr, and (c) anodic peak potential  $E_{pa}$  ( $\blacktriangle$ ) representing Trp and ( $\bullet$ ) Adr as a function of pH for the CM/AgNPs/MWCNT/GCE in phosphate buffered solutions containing  $2.0 \times 10^{-4}$  M of analytes.

The voltammograms for 200 M Adr and Trp in 0.1 M phosphate buffer solution at different scan rates are shown in Fig. 4. Within the examined range, oxidation ( $I_{pa}$ ) linearly increased with the squared of scan rate (Fig. 4d and 4e), with  $I_p(\mu A) = 5E-07v + 2E-05$  ( $R^2 = 0.9957$ ) and  $I_p(\mu A) = 2E-06v + 3E-06$  ( $R^2 = 0.979$ ) for Trp and Adr, respectively. The relationship between  $I_{pa}$  and scan rate was also linear (see Fig. 3S). The findings showed that the Trp and Adr electrode processes at the CMNPs/AgNPs/MWCNT/GCE electrode are diffusion and adsorption controlled.

Using Laviron's equation, cyclic voltammetry was used to determine the charge transfer coefficient ( $\alpha$ ) and apparent heterogeneous charge transfer rate constant ( $k_s$ ) for electron transport between the modified electrode and a redox pair of Trp. The  $k_s$  and  $\alpha$  values were  $3842.92 \pm 70.8 \text{ s}^{-1}$  and 0.3, respectively.

According to the results, the modified electrode surface serves as an electrocatalyst, improves the electrochemical detection of targets, and increases the sensitivity and selectivity of determination. This consents with the mechanism of an EC', in which the electrochemical reaction is effectively controlled by the electrode surface. Furthermore, peak currents for Trp and Adr at the modified electrode were found to be higher than those obtained at the bare GCE, indicating that the electrode surface actively catalyzes the electrochemical oxidation of the analytes. Also, the enhanced kinetics of the electrochemical processes at the modified electrode are observed by the shift of oxidation peaks to less positive potentials, which was probably made possible by the changed surface. A synergistic effect is produced on the electrode surface by the coexistence of MWCNTs, AgNPs, and CMNPs. This effect improves conductivity, offers active sites for adsorption, and may even catalyze the oxidation processes of Trp and Adr. Along with the study using Laviron's equation, the linear connection between peak current and scan rate implies that the electrochemical processes at the modified electrode are

diffusion-controlled, further confirming an EC' mechanism in which the electrode surface supports electron transport.

**Optimization of AgNPs amounts.** At pH 3, and a scan rate of  $100 \text{ mV s}^{-1}$ , the responses of a modified electrode containing various quantities of AgNPs, ranging from 2 to  $15 \mu\text{l}$ , were examined. According to the findings, increasing the nanoparticle concentration to  $10 \mu\text{l}$  improved the peak current. There was little difference in peak currents after adding  $10 \mu\text{l}$  of AgNPs. As a result, a volume of  $10.0 \mu\text{l}$  silver nanoparticles was chosen to achieve the maximum sensitivity. Because, AgNPs may aggregate at high volumes, reducing the active surface area of the nanocomposite and, as a result, lowering peak currents significantly.

### Calibration Graphs of the Analyte Using CMNPs/AgNPs/MWCNT/GCE Electrode

After optimization of the experimental condition, the applicability of the proposed nanocomposite was investigated by selective determination of analytes. Therefore, a differential pulse voltammogram of various concentrations of one analyte in the presence of a constant concentration of another analyte was measured and the relationship between the  $I_{pa}$  and the concentration was considered (Fig. 4S). The calibration curves were plotted at 0.860 and 0.421 V for Trp and Adr, respectively. The calibration graphs were developed and calibration equations, correlation coefficients, and detection limits were obtained (see Table 1). The findings reveal that the system is quite sensitive when determining Trp and Adr at the same time.

The repeatability of the modified electrode was further tested through repetitive recording of DPV signals at a fixed concentration of 200 mM for each analyte. The RSD of peak current intensity was 2.5 percent for Trp and 3.1 percent for Arg. The modified GCE response is highly repeatable, according to these results. In storage stability tests with 200 mM of targets using a modified electrode, peak current

**Table 1.** Analytical Features of the Calibrations Obtained with the CMNPs/AgNPs/MWCNT/GCE Electrode

Analyte	Calibration equation	$R^2$	LDR ( $\mu\text{M}$ )	LOQ ( $\mu\text{M}$ )
Adr	$I/\mu A = 4 \times 10^{-8} C_{\text{Adr}} + 5 \times 10^{-6}$	0.998	1.0-1150	0.058
Trp	$I/\mu A = 6 \times 10^{-8} C_{\text{Trp}} + 7 \times 10^{-6}$	0.995	0.5-1200	0.032

did not change substantially over the first 16 days and only decreased by roughly 7% after 25 days.

### Interference Study

In order to evaluate the selectivity of the proposed electrode foreign species that can influence the determination of adrenaline and tryptophan, were studied. The species were selected that are usually present with adrenaline and tryptophan in biological fluids or pharmaceutical products. The limit of tolerance was considered to be the concentration of the external agent which caused a relative error of about 10.0% in the determination of 75 mM of Trp and Adr. The results show that the manufactured electrode is selective and is very suitable for simultaneous measurement of Trp and Adr (Table 2). Only small amounts of leucine will interfere with tryptophan measurements.

### Applications of the Method to Real Samples

Analytes in various urine and adrenaline injection samples were determined to confirm the applicability of the suggested approach. Triplet measurements were used for all analyses. Before analysis, the Adr injection solutions were

**Table 2.** Effect of Different Interferences on DPV Peak of Adr and Trp

Interfering ion	Tolerance limit ( $\mu\text{M}$ )	
	Adr	Trp
Leucine	1000	5
Phenylalanine	600	300
Arginine	200	200
Aspartic acid	600	200

thirty times diluted. According to the findings, the proposed nanocomposite can be utilized to determine analytes simultaneously in biological samples with good results. Other approaches for determining Adr and Trp were also used to compare the response properties of the suggested electrode (see Table 3). In comparison to some of the previously reported electrodes, these features reveal that the nanocomposite has a higher sensitivity, a lower detection limit, and a larger linear range (Table 4).

### CONCLUSION

Because adequate amounts can improve hunger, sleep patterns, and mood swings in the brain, tryptophan is utilized as a supplement to modulate its levels in the human body. Adrenaline levels, both low and high, have a significant impact on the functioning of biological systems. As a result, determining the concentration of analytes is critical for increasing our understanding of neurophysiology, as well as the clinical diagnosis of various disorders and the development of control medicines in drug research. By using a sensitive oxidation procedure at pH 3, a very sensitive electrochemical method for determining Trp and Adr was developed. The synergistic effect of CMNPs, AgNPs, and MWCNTs, which not only provided quick electron transport but also showed excellent electrochemical enhancement, is responsible for oxidation enhancement. Because target species might connect with both carbon chains and curcumin chain and be trapped on the porous surface via hydrophobic contact and electrostatic attraction. The approach has been used to determine Trp in human urine and commercial adrenaline injections. The results show that the method may be used to determine the concentrations of Trp and Adr in actual samples.

**Table 3.** Calculated Recovery Values of Urine and Injection Samples

Samples	Added ( $\mu\text{M}$ )		Found ( $\mu\text{M}$ )		Recovery (%)	
	Adr	Trp	Adr	Trp	Adr	Trp
Urine sample	93.45	96.1	92.1	96.3	98.6	100.2
Urine sample	190.0	190.0	190.8	190.5	100.4	100.2
Urine sample	270.3	277	266.1	274.5	98.5	99.1
Injection solution of Adr	650.0	200.0	644.0	210.0	99.2	103.3
Injection solution of Adr	300.0	300.0	309.5	303.5	103.2	101.2



**Table 4.** Characteristic Comparison of some Reported Works for the Determination of Analytes with the Proposed Method

Modifier	Detection limit		Dynamic range		Technique	Ref.
	(μM)		(μM)			
	Trp	Adr	Trp	Adr		
CMNPSWCNT_CPE <sup>a</sup>	-	0.2	-	0.63-8.86; 8.86-111.1; 111.1-714.2	DPV	1
(AuNPs/poly(NDI)/GCE <sup>b</sup>	0.09	0.009	3.0-632.0	0.01-680.0	DPV	2
Alumina/graphene/Cu hybrids	0.009	0.027	1-1200	1-1000	CV	18
Graphite screen-printed electrode	-	0.5	-	1.0-900.0; 1.0-1200.0	DPV	7
CMNPs/AgNPs/MWCNT/GCE	0.032	0.058	0.5-1200	1.0-1150	DPV	Current study

<sup>a</sup>Coumestan derivative and multiwall carbon nanotubes modified carbon paste electrode. <sup>b</sup>Au nanoparticles/poly 5-[(2-hydroxynaphthalen-1-yl)diazanyl] isophthalic acid film.

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