

# An Electrochemical Sensor Based on MB/Ag-ZnO/Graphene Modified Glassy Carbon Electrode for Determination of L-Tryptophan in Biofluid Samples

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In this work, graphene (GR) and Ag-ZnO nanocomposites were prepared and used together with methylene blue (MB) as electrode materials to modify a glassy carbon electrode (GCE). The electrochemical behavior of L-tryptophan (L-Trp) on the fabricated MB/Ag-ZnO/GR/GCE was investigated by cyclic voltammetry and differential pulse voltammetry. MB/Ag-ZnO/GR clearly enhanced the electrochemical oxidation of L-Trp. In a 0.1 mol/L phosphate buffer solution at pH 4.0, the peak current response at the modified electrode increased linearly with an increase in the L-Trp concentration from  $2.0 \times 10^{-6}$  to  $1.4 \times 10^{-4}$  mol/L, and the detection limit (S/N = 3) was  $1.0 \times 10^{-6}$  mol/L. The electrode showed good reproducibility, stability, and selectivity. The sensor was used for the determination of L-Trp in biofluid samples (pig serum and pig urine), and the recovery rate ranged from 97.1% to 104.2%. The fabricated electrode was proposed for the electrochemical analysis of L-Trp, indicating the potential for practical applications in the biological field.

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**Keywords:** Graphene, Ag-ZnO nanocomposites, L-Tryptophan, Methylene blue

## 1. INTRODUCTION

L-tryptophan (L-Trp) is an essential amino acid in the human body used for synthesis of proteins [1]. L-Trp is also indispensable for establishing and maintaining a positive nitrogen balance in human nutrition. As L-Trp is scarcely present in vegetables, it is sometimes added in diets and foods, as well as in pharmaceutical preparations, to eliminate dietary defects [2]. Moreover, the level of L-Trp in plasma is closely related to the severity of liver disease [3]. Monitoring of L-Trp, L-cysteine, and other nitrogen-containing molecules is imperative in food processing, biochemistry, clinical analysis,

and other fields [4-10]. Therefore, it is of great significance to establish a simple, sensitive, and selective method for L-Trp detection. Up to now, various instrumental methods, including high-performance liquid chromatography [11-13], capillary electrophoresis [14-16], fluorescence spectroscopy [17], flow injection with chemiluminescence detection [18], and UV-visible absorption spectrophotometry [19], have been developed for the determination of L-Trp content in pharmaceutical preparations or biological samples. However, these methods generally require expensive instrumentation and complicated pretreatment processes. Recently, electrochemical methods, which offer the advantages of simple instrumentation, low detection cost, and fast response, have attracted much interest in L-Trp analysis. Wen et al. [20] have synthesized a graphene hybrid tube-like structure for L-Trp detection. Deng et al. [21] have employed a reduced-graphene-oxide-modified glassy carbon electrode to detect L-Trp. Fan et al. [22] have modified a glassy carbon electrode with Nafion and TiO<sub>2</sub>-graphene for the detection of Trp. Xu et al. [23] have proposed chiral recognition of Trp enantiomers using a  $\beta$ -cyclodextrin-platinum nanoparticle/graphene nanocomposite-modified electrode. In addition, a composite of triangular gold nanoplates combined with graphene oxide (GO) and Nafion has been demonstrated to show sensitive response to L-Trp [24].

Because of its extraordinary electron transport properties and high electrocatalytic activity, graphene (GR) can greatly promote electrochemical reactions on the surface of modified electrodes [25-28]. GR-based electrochemical sensors have shown excellent analytical performance for biomolecular detection [29-32]. Moreover, the unique two-dimensional structure of GR makes it an attractive carrier material for metal-oxide-catalyst nanoparticles [33, 34]. Composites of GR and metal oxides have been employed as reinforced materials for the construction of electrochemical sensors [35].

On the other hand, ZnO is a well-known semiconductor that has received considerable research interest due to its low cost, high stability, and outstanding photocatalytic performance [36-39]. However, electron transfer in ZnO is slow because of its semiconducting characteristics. Thus, various metal nanoparticles possessing high conductivity have been incorporated in ZnO to improve its performance. Silver, which is the most highly conducting material, has been doped in ZnO to prepare Ag-ZnO nanocomposites, showing enhanced photocatalytic performance [40].

As a polynuclear aromatic compound with excellent electrochemical activity, methylene blue (MB) has been extensively utilized as a redox mediator to modify electrodes for developing electrochemical sensors. However, due to its low molecular weight, MB is weakly adsorbed on bare electrodes and may be easily lost through desorption. To overcome this problem, loading of MB onto electrodes modified with various nanomaterials, such as Cu<sub>2</sub>O [41], SiO<sub>2</sub> [42], and TiO<sub>2</sub> [43, 44], has been demonstrated. The large surface area of these nanomaterials provides effective adsorption sites for MB loading.

This work aims to develop a novel electrochemical sensor using a glassy carbon electrode (GCE) modified by GR, Ag-ZnO, and MB for the sensitive and selective detection of L-Trp. Because of the excellent electrochemical performance of MB/Ag-ZnO/GR, enhanced voltammetric response to L-Trp was observed on the modified electrode. Based on such a modified electrode, a high-performance electrochemical sensor for the detection of L-Trp in biofluids was demonstrated.

## 2. EXPERIMENTAL

### 2.1 Chemicals and apparatus

GO was purchased from Nanjing Jicang Nano Technology Co., Ltd. (Nanjing, China). Poly(dimethyl diallyl ammonium chloride) (PDDA, relative molecular mass 200,000–350,000, quality score of 20%) was purchased from Aldrich (USA). MB was obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Pig serum samples were provided by the Institute of Subtropical Agriculture, Chinese Academy of Sciences. Electrochemical measurements were conducted in a conventional three-electrode cell controlled by a CHI760B potentiostat (Shanghai Chenhua Instrument Co., Ltd.). All potentials were obtained versus a Ag/AgCl (saturated KCl solution) reference electrode.

### 2.2 Preparation of GR

GR was prepared with GO based on a previously described method [30]. Briefly, 10.0 mg of GO was dispersed in 10.0 mL of H<sub>2</sub>O. Then, 0.4 mL of PDDA was added, and the mixture was stirred for 30 min. Afterwards, 0.4 mL of hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>) was added. The mixture was stirred for 10 min and heated at 120 °C for 24 h. The obtained GR was rinsed with ultrapure water, dried at 80 °C, and ground into a powder for use.

### 2.3 Preparation of Ag-ZnO/MB composites

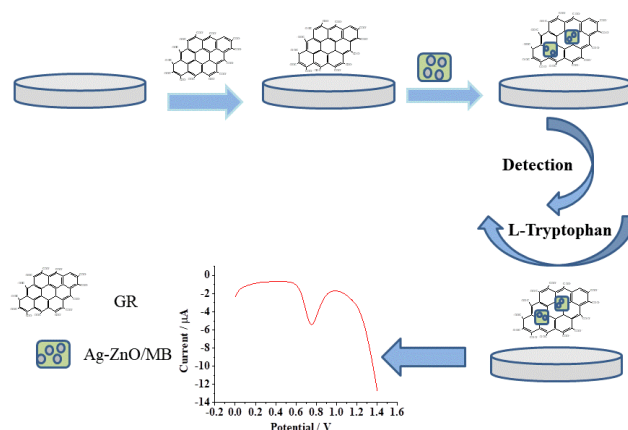
The preparation of ZnO is outlined as follows. First, 4.0 mL of 1 mol/L zinc sulfate and 4.0 mL of 1 mol/L CTAB were dissolved in 400 mL of water in a 500-mL beaker. The beaker was placed in 80 °C water for 5 h. Then, 1.6 mL of concentrated ammonia solution was added directly into this beaker, and the solution pH was maintained at about 10. The obtained zinc oxide precipitate was collected and washed with water for several times, and then dried in air.

To prepare Ag-ZnO, 10 mg of ZnO powder was dispersed in 10.0 mL of water in a 100-mL beaker by sonication for 30 min. Then, 10.0 mL of silver nitrate (0.01 mol/L) was added to the dispersed ZnO solution. The entire solution was stirred for 2 h so that Ag<sup>+</sup> was sufficiently adsorbed onto the surface of ZnO. The Ag<sup>+</sup>-adsorbed ZnO precipitate was collected and washed several times with water, and then re-dispersed in 20.0 mL of water. After 0.2 mL of hydrazine hydrate solution (1 mol/L) was added, a yellow Ag-ZnO precipitate formed. The product was collected and washed several times with water and dried. To prepare Ag-ZnO/MB, 12.0 mg of Ag-ZnO nanoparticles and 4.0 mg of MB were dispersed in 5.0 mL of water with the aid of a 2-h ultrasonication.

### 2.4 Electrode modification

Figure 1 shows the schematic illustration for the fabrication of the modified electrode. Prior to modification, the GCE was polished to a mirror surface with 0.1-, 0.3-, and 0.05- $\mu\text{m}$   $\alpha\text{-Al}_2\text{O}_3$  powder,

and ultrasonically washed with ultrapure water, ethanol, and ultrapure water, respectively. First, 5  $\mu\text{L}$  of GR dispersion was coated onto the surface of GCE. After drying, the surface of the GR/GCE was coated with 5  $\mu\text{L}$  of Ag-ZnO/MB dispersion. The obtained MB/Ag-ZnO/GR/GCE was dried before electrochemical measurements.



**Figure 1.** Schematic illustration for the fabrication of MB/Ag-ZnO/GR/GCE

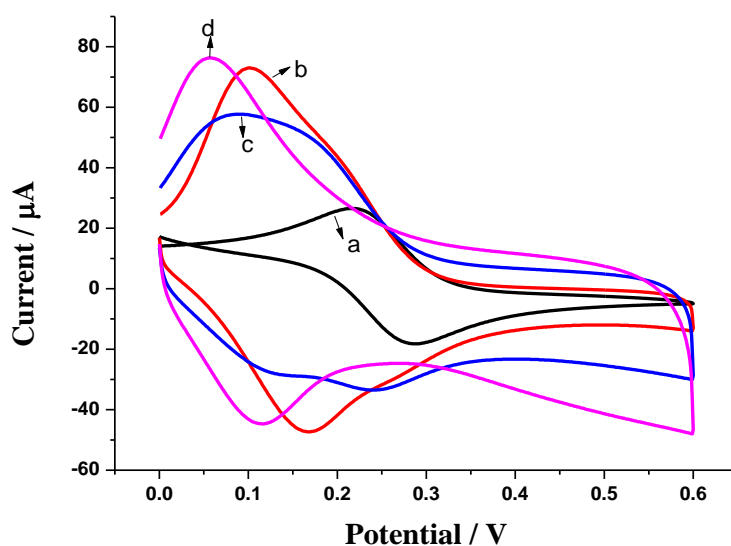
### 2.5 Sample preparation

Pig serum and pig urine samples were provided by the Institute of Subtropical Agriculture of the Chinese Academy of Sciences (Changsha). Six different kinds of pig serum and pig urine samples were centrifuged at 8000 rev/min for 10 min, and the supernatant (100.0  $\mu\text{L}$ ) was added to the pH 4.0 phosphate buffer solution (PBS) (0.1 mol/L) for dilution. Different concentrations of L-tryptophan were added to the treated pig serum or urine sample solution and measured with a modified electrode.

## 3. RESULTS AND DISCUSSION

### 3.1 Electrochemical characterization

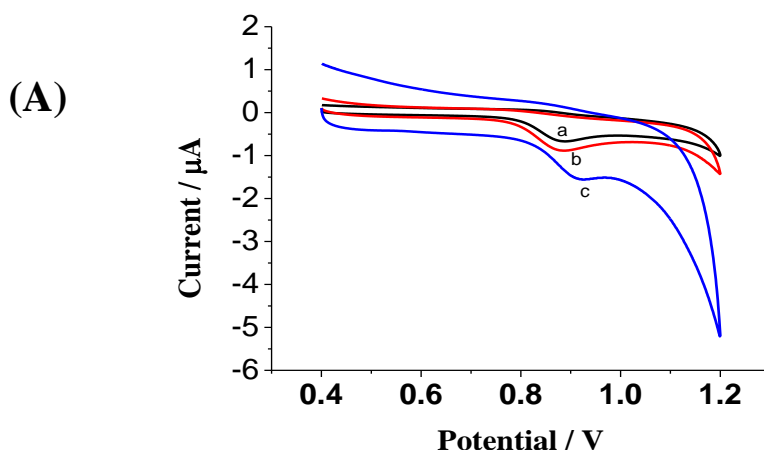
The electrochemical characteristics of the bare GCE and different modified electrodes such as GR/GCE, GR/Ag-ZnO/GCE, and MB/Ag-ZnO/GR/GCE were evaluated by cyclic voltammetric (CV) measurements in  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  solution (Figure 2). Compared with the bare GCE, the GR and Ag-ZnO modified electrodes show enhanced peak currents for the  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox reaction, which can be due to the enhanced electron transfer ability and large surface area of GR [28], and the excellent physicochemical performance of Ag-ZnO [40]. In the case of the MB/Ag-ZnO/GR/GCE, the redox peak currents of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  are further enhanced due to the high electrocatalytic activity of MB [45]. The anodic peak current on MB/Ag-ZnO/GR/GCE is 3.5, 1.04, and 1.3 times that on GCE, GR/GCE, and Ag-ZnO/GR/GCE, respectively. This result indicates that MB/Ag-ZnO/GR delivers the best electrochemical performance to promote electron transfer on the electrode.

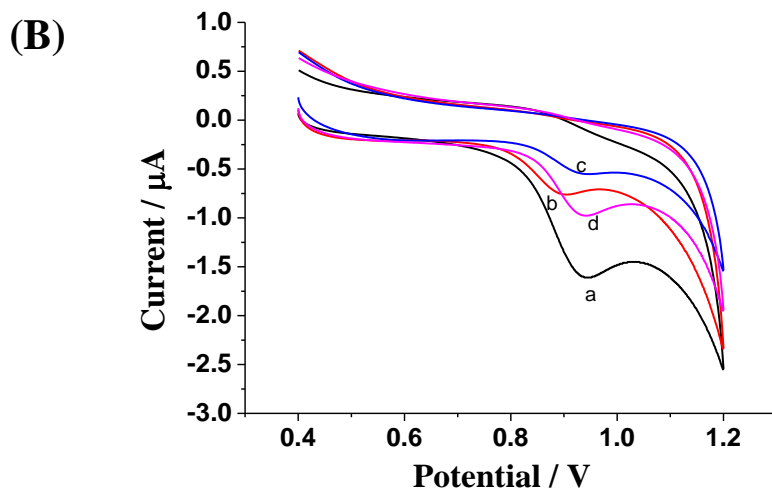


**Figure 2.** CV curves recorded on (a) GCE, (b) GR/GCE, (c) Ag-ZnO/GR/GCE, and (d) MB/Ag-ZnO/GR/GCE in a 0.1-mol/L KCl solution containing 1.0 mmol/L  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ .

### 3.2 Electrocatalytic oxidation of L-Trp on modified electrodes

The electrochemical responses of L-Trp on bare GCE and various modified electrodes were investigated in 0.1-mol/L PBS at pH 6.0 (Figure 3A). On bare GCE, only one anodic peak appears near 0.85 V in the CV curve, recorded in the sweeping potential range of 0.4 to 1.2 V. The response is similar to the previous result observed by Deng et al. [21], indicating that L-Trp undergoes an irreversible oxidation process on the electrode. After Ag-ZnO/GR- or MB/Ag-ZnO/GR-modified GCE is applied, the oxidation peak current is increased, demonstrating the advantage of modified electrodes in the promotion of the electrochemical response to L-Trp. Further observation shows that the oxidation peak current of L-Trp on MB/Ag-ZnO/GR/GCE is higher than that on bare GCE or Ag-ZnO/GR/GCE. This is mainly due to the addition of the electroactive MB on the Ag-ZnO/GR material, which can catalyze the oxidation of L-Trp.

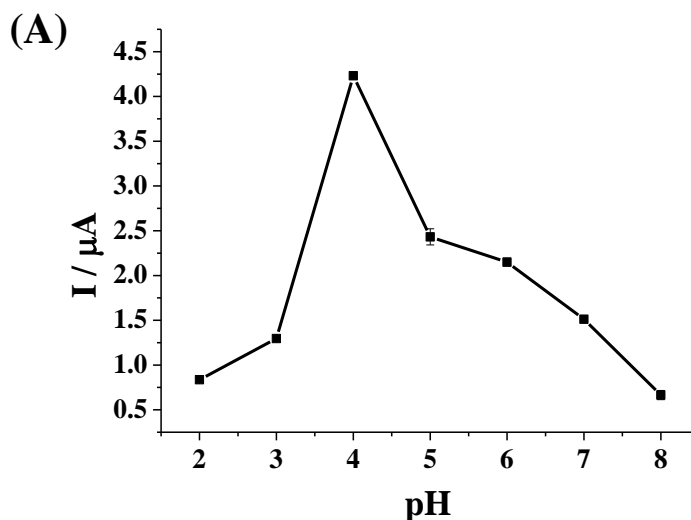


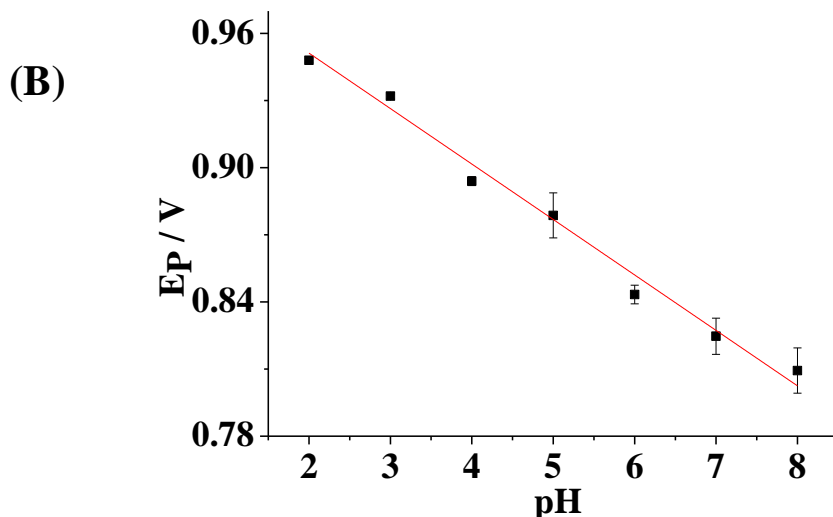


**Figure 3.** (A) CV curves recorded on (a) GCE, (b) Ag-ZnO/GR/GCE, (c) MB/Ag-ZnO/GR/GCE in 0.1-mol/L PBS (pH = 6.0) containing  $1.0 \times 10^{-5}$  mol/L L-Trp. (B) CV curves recorded in 0.1-mol/L PBS (pH = 6.0) containing  $1.0 \times 10^{-5}$  mol/L L-Trp on MB/Ag-ZnO/GR/GCE, prepared with different ratios of Ag-ZnO to MB: (a) 3:1, (b) 4:1, (c) 2:1, and (d) 1:1.

Moreover, the ratio of Ag-ZnO to MB in the modified electrode is observed to influence the electrochemical response of L-Trp. Figure 3B shows that when the ratio of Ag-ZnO to MB in the modified electrode is changed from 4:1 to 1:1, the electrochemical oxidation peak current of L-Trp varies. The optimal ratio of Ag-ZnO to MB is found to be 3:1, which exhibits the highest oxidation peak current. Accordingly, 3:1 for Ag-ZnO:MB was selected to fabricate the modified electrode in this study.

### 3.3 Effects of pH and scan rate

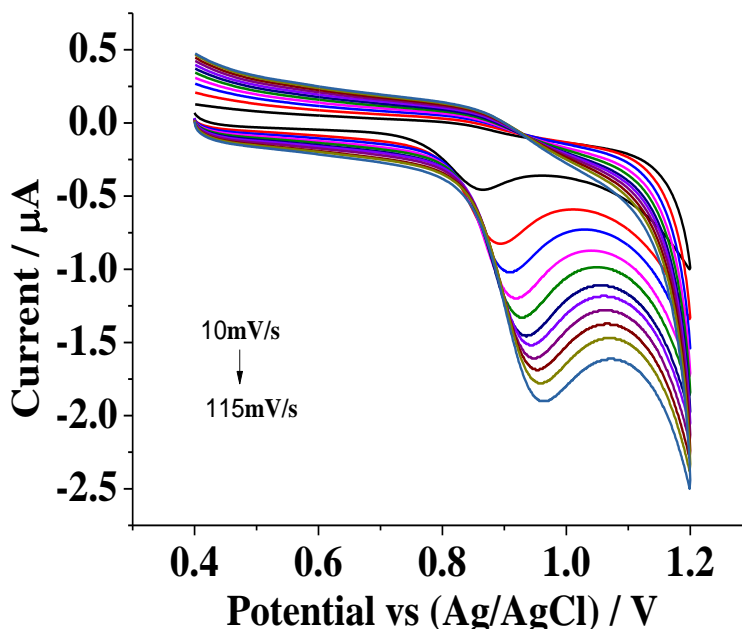




**Figure 4.** Effect of pH on (A) oxidation peak current and (B) oxidation peak potential of L-Trp on MB/Ag-ZnO/GR/GCE.

To study the pH effect on the oxidation of L-Trp, the electrochemical responses of MB/Ag-ZnO/GR/GCE to  $1.0 \times 10^{-5}$  mol/L L-Trp were recorded by differential pulse voltammetry (DPV) in 0.1-mol/L buffer solutions at different pH. Figure 4 shows the influence of pH on the oxidation peak current and potential of L-Trp, respectively. As can be seen in Figure 4A, when the pH of the buffer solution is changed from 2.0 to 4.0, the peak current of L-Trp gradually increases. However, when the pH further increases from 4.0 to 8.0, the peak current gradually decreases. Therefore, pH 4.0 was selected as the optimal pH condition for the detection of L-Trp.

Figure 4B shows that pH is well linearly correlated with the oxidation peak potential ( $E_p$ ) of L-Trp, meaning that proton transfer is involved in the oxidation of L-Trp. The linear fitting equation can be expressed as  $E_{pa}/V = 1.0008 - 0.02479\text{pH}$ , with a linear correlation coefficient  $R = 0.9739$ . According to the Nernst equation  $E_p = E_0 - 0.059(m/n)\text{pH}$ , where  $m$  is the number of protons in the electrode reaction, and  $n$  is the number of electrons transferred in the electrode reaction. From the slope of the oxidation peak potential of L-Trp versus pH,  $m/n = 0.42$  can be obtained. This result indicates that in the electrochemical oxidation of L-Trp on MB/Ag-ZnO/GR/GCE, one proton is involved in a two-electron transfer reaction, different from the two-proton and two-electron process of L-Trp on reduced-graphene-oxide-modified GCE [21] or Nafion/TiO<sub>2</sub>-GR-modified GCE [22]. This difference might be due to the catalytic oxidation of L-Trp by MB, studied in the present work.



**Figure 5.** CV curves recorded on MB/Ag-ZnO/GR/GCE in 0.1-mol/L PBS (pH = 4) containing  $1.0 \times 10^{-5}$  mol/L L-Trp at different scan rates.

On the other hand, the electrochemical behavior of L-Trp on Ag-ZnO-MB/GR/GCE was investigated by CV at different scan rates (Figure 5). The result shows that the oxidation peak potential is linear to the logarithm of the sweep rate ( $\nu$ ). The linear equation is  $E_{pa} = 0.08732 \log \nu + 0.07676$  ( $R = 0.9989$ ). According to the Laviron formula

$$E_{pa} = E^{0'} + \frac{2.303RT}{\alpha nF} \lg \frac{RTk^0}{\alpha nF} + \frac{2.303RT}{\alpha nF} \lg \nu \quad (1)$$

where  $E^{0'}$  is the formula potential,  $\alpha$  is the transfer coefficient,  $n$  is the electron transfer number,  $F$  is the Faraday constant,  $k^0$  is the standard heterogeneous reaction rate constant,  $R$  is the molar gas constant,  $T$  is the temperature, and  $D$  is the diffusion coefficient. When  $\alpha = 0.4-0.6$  for an irreversible electrode reaction at normal temperature is used,  $n$  is calculated to be approximately 1 for the oxidation of L-Trp. This result shows that one electron is transferred in the oxidation process of L-Trp on MB/Ag-ZnO/GR/GCE.

### 3.4 Voltammetric sensing of L-Trp

Figure 6A shows the DPV responses of MB/Ag-ZnO/GR/GCE to L-Trp at different concentrations. The oxidation peak current is found to increase linearly with increasing the concentration of L-Trp from  $2.0 \times 10^{-6}$  to  $1.4 \times 10^{-4}$  mol/L (Figure 6B). The linear regression equation is expressed as  $I_{pa} (\mu A) = 0.0012 + 0.04297C (\mu mol/L)$ , with  $R^2 = 0.9941$ . The detection limit estimated by the method of  $3S/N$  is  $1.0 \times 10^{-6}$  mol/L. Table 1 lists the electrochemical sensors for L-Trp detection based on different electrodes. The proposed sensor based on the MB/Ag-ZnO/GR/GCE



exhibits a wider linear range and lower detection limit as compared with many of the reported electrochemical sensors for L-Trp.

To evaluate the reproducibility of the proposed sensor, the voltammetric responses of six modified electrodes prepared in the same batch to  $1.0 \times 10^{-5}$  mol/L L-Trp were tested. The relative standard deviation (RSD) was found to be 3.8%, demonstrating that the sensor has good reproducibility. Moreover, the voltammetric curves of L-Trp of  $1.0 \times 10^{-5}$  mol/L were continuously measured six times using the same modified electrode. The result of RSD is 2.0%, showing good repeatability. Meanwhile, the stability of the modified electrode was tested by checking the voltammetric current of  $1.0 \times 10^{-5}$  mol/L L-Trp on MB/Ag-ZnO/GR/GCE every other day. As shown in Figure 7, the current signal of the modified electrode to L-Trp still retain 82% of its original response after 24 d, indicating that the modified electrode has good stability.

**Table 1.** Comparison of electrochemical sensors for L-Trp detection based on different electrodes.

Electrode	Method	Linear range (mol/L)	Detection limit (mol/L)	Reference
ERGO <sup>a</sup> /GCE	DPV	$2.0 \times 10^{-7}$ – $4 \times 10^{-5}$	$1.0 \times 10^{-7}$	[21]
Nafion/TiO <sub>2</sub> -GR/GCE	DPV	$5.0 \times 10^{-6}$ – $1.4 \times 10^{-4}$	$7.0 \times 10^{-7}$	[22]
$\beta$ -CD-PtNPs/GNs <sup>b</sup> /GCE	DPV	$5.0 \times 10^{-5}$ – $5.0 \times 10^{-3}$	$1.7 \times 10^{-5}$	[23]
4FEPE <sup>c</sup> /CPE <sup>d</sup>	CV	$6.0 \times 10^{-6}$ – $3.3 \times 10^{-3}$	$1.8 \times 10^{-6}$	[46]
CPE	DPV	$2.0 \times 10^{-3}$ – $3.0 \times 10^{-2}$	$1.7 \times 10^{-6}$	[47]
Boron-doped diamond	DPV	$4.0 \times 10^{-4}$ – $1.0 \times 10^{-3}$	$1.0 \times 10^{-5}$	[48]
FePt/CNTs <sup>f</sup> /CPE	SWV <sup>j</sup>	$5.0 \times 10^{-6}$ – $5.0 \times 10^{-4}$	$1.0 \times 10^{-6}$	[49]
MMWCNTPE <sup>g</sup>	SWV	$1.0 \times 10^{-6}$ – $4.0 \times 10^{-4}$	$8.2 \times 10^{-7}$	[50]
VFMWCNTPE <sup>h</sup>	SWV	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	$1.0 \times 10^{-6}$	[51]
GNP/CILE <sup>i</sup>	SWV	$5.0 \times 10^{-6}$ – $9.0 \times 10^{-4}$	$4.0 \times 10^{-6}$	[52]
MB/Ag-ZnO/GR/GCE	DPV	$2.0 \times 10^{-6}$ – $1.4 \times 10^{-4}$	$1.0 \times 10^{-6}$	This Work

<sup>a</sup> ERGO: electrochemically reduced graphene oxide.

<sup>b</sup>  $\beta$ -CD-PtNPs/GNs:  $\beta$ -cyclodextrin, platinum nanoparticles and GR.

<sup>c</sup> 4FEPE: 1-[4-ferrocenyl ethynyl] phenyl]-1-ethanone.

<sup>d</sup> CPE: carbon-paste electrode.

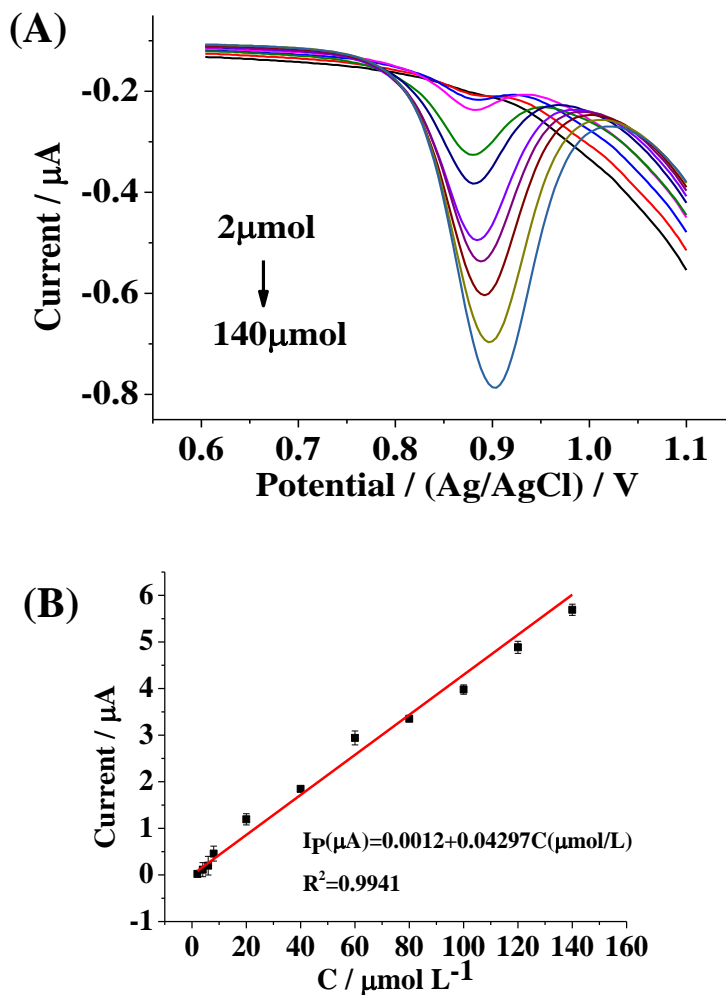
<sup>f</sup> CNTs: carbon nanotubes.

<sup>g</sup> MMWCNTPE: modified multiwall carbon-nanotube-paste electrode.

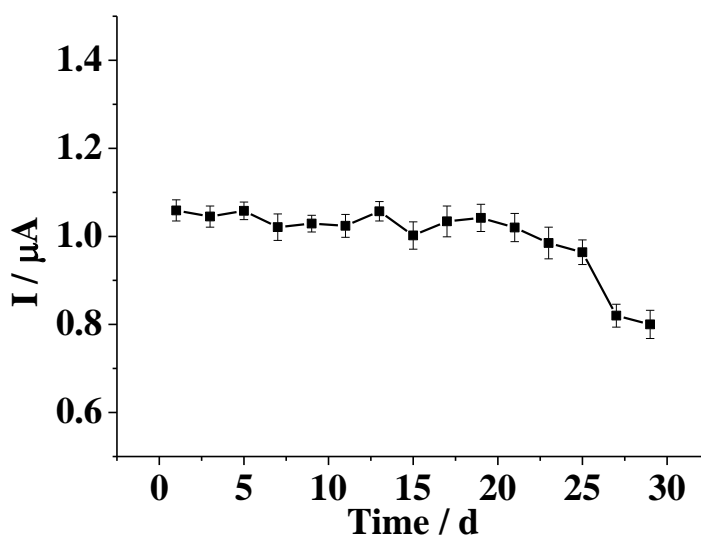
<sup>h</sup> VFMWCNTPE: vinylferrocene-modified carbon-nanotube-paste electrode.

<sup>i</sup> GNP/CILE: carbon ionic liquid electrode modified with gold nanoparticle.

<sup>j</sup> SWV: square-wave voltammetry.



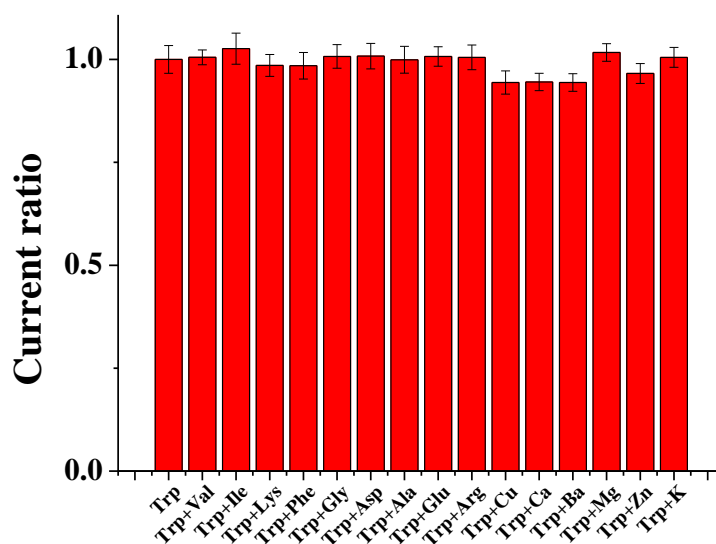
**Figure 6.** (A) DPV curves of MB/Ag-ZnO/GR/GCE in 0.1-mol/L PBS (pH = 4.0) containing L-Trp at different concentrations. (B) Linear relationship between oxidation peak current and L-Trp concentration.



**Figure 7.** Stability of MB/Ag-ZnO/GR/GCE for determination of  $1.0 \times 10^{-5}$  mol/L L-Trp for 30 d.

3.5 Effect of interfering substance on MB/Ag-ZnO/GR/GCE

On the other hand, the responses of MB/Ag-ZnO/GR/GCE to  $2.0 \times 10^{-5}$  mol/L L-Trp in the presence of 50-fold concentration of other substances were studied. The selected substances are common amino acids and metal ions in living organisms, such as L-arginine (Arg), L-glycine (Gly), L-alanine (Ala), L-valine (Val), L-isoleucine (Ile), L-lysine (Lys), L-phenylalanine (Phe), aspartic acid (Asp), L-glutamic acid (Glu),  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{K}^+$ . As shown in Figure 8, all these substances have almost no obvious interference in the determination of L-Trp. Therefore, this modified electrode has good selectivity and can be used for the determination of L-Trp in real samples.



**Figure 8.** Influences of interfering substances on the voltammetric current response of L-Trp on MB/Ag-ZnO/GR/GCE.

3.6 Application of MB/Ag-ZnO/GR/GCE to determination of L-Trp in biofluid samples

**Table 2.** Determination of L-Trp in pig serum and pig urine samples.

Sample	Initial value ( $\mu\text{mol/L}$ )	Spiked ( $\mu\text{mol/L}$ )	Found ( $\mu\text{mol/L}$ )	Recovery (%)	RSD (%)
a	37.07	0.14	50.75	97.7	3.3
b	39.42	0.12	51.57	101.2	1.4
c	46.49	0.10	56.36	98.7	2.8
d	37.66	0.08	45.40	96.8	5.7
e	38.28	0.06	44.49	103.4	5.4
f	47.63	0.04	51.80	104.2	5.2
g	38.42	0.14	52.38	99.7	4.1
i	41.39	0.10	51.22	98.3	4.3
j	39.95	0.08	47.82	98.3	1.4
k	47.04	0.06	52.97	98.9	1.8
l	58.89	0.04	62.81	97.9	2.1

The contents of L-Trp in biofluid samples including pig serum (a–f) and pig urine (g–l) were determined by the proposed method on MB/Ag-ZnO/GR/GCE. Moreover, the standard addition method was used by adding different concentrations of standard L-Trp to the treated pig serum and pig urine samples. Table 2 shows that the recovery values are in the range of 97.1%–104.2%, indicating that MB/Ag-ZnO/GR/GCE has good accuracy in the determination of L-Trp in biofluid samples.

#### 4. CONCLUSIONS

In this work, we fabricated an MB/Ag-ZnO/GR/GCE to study the electrochemical behavior of L-Trp. This modified electrode was found to be effective in enhancing the voltammetric response of L-Trp. The influence of pH and scan rate on voltammetric behavior of L-Trp on the MB/Ag-ZnO/GR/GCE was investigated and analyzed. Under the optimal conditions, the MB/Ag-ZnO/GR/GCE exhibited a voltammetric current proportional to the L-Trp concentration in the range of  $2.0 \times 10^{-6}$  to  $1.4 \times 10^{-4}$  mol/L, with a detection limit (3S/N) of  $1.0 \times 10^{-6}$  mol/L. The modified electrode was successfully applied to the detection of L-Trp in biofluid samples of pig serum and pig urine, with satisfactory accuracy. Therefore, the proposed sensor based on the MB/Ag-ZnO/GR/GCE has potential practical applications for L-Trp detection.

#### CONFLICT OF INTEREST

The author declares no conflict of interest, financial or otherwise.

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