

RESEARCH PAPER

Development of a rapid and sensitive electrochemical sensing assay by applying metal-organic framework/multi-walled carbon nanotubes (MOF/MWCNTs) for determination of ascorbic acid

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ABSTRACT

Objectives: L-ascorbic acid (AA, vitamin C), has important bodily functions, including immune defense, collagen formation, and metabolism. Symptoms of many diseases like cancer or cardiovascular disorders can be observed owing to maladjustment or deficiency. Hence, developing sensitive and rapid methods to determine AA in biological samples is essential. In this study, a novel electrochemical sensing assay based on Zn metal-organic framework embedded in multi-walled carbon nanotubes (Zn-MOF/MWCNTs) has been effectively developed to modify glassy carbon electrode (GCE).

Materials and Methods: Zn-MOF was synthesized using the solvothermal technique and mixed with multi-walled carbon nanotubes to obtain a modifier suspension. Various characterization methods including XRD (X-ray Diffraction), EDX (Energy-dispersive X-ray spectroscopy), HR-TEM (High-resolution transmission electron microscopy), FT-IR (Fourier-transform infrared spectroscopy), and FESEM (Field emission scanning electron microscopy) were applied to confirm the proper synthesis of Zn-MOF. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) approaches were employed to study the electrochemical behavior of the modified GCE and electrochemical determination of AA with high sensitivity.

Results: Under the optimized conditions including the drop volume, supporting electrolyte type and concentration, buffer type and concentration, and pH, the linear range and LOD (detection limit) were acquired 2–22 μM equal to 1.211 μM respectively. Moreover, other prominent analytical features including repeatability, stability, and high reproducibility were investigated for the proposed sensing platform. Additionally, the prepared sensor was effectively utilized for determination of AA in human plasma samples, attaining a recovery of 93.1%.

Conclusion: These findings clearly confirm that the developed Zn-based MOF/MWCNT sensing assay is a promising platform for accurate and effective AA determination in real biological samples, and confirms its potential for feasible biomedical applications.

Keywords: Ascorbic acid; Electrochemical sensing assay; Zn-based Metal-organic framework; Multi-walled carbon nanotubes; Modified electrodes

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INTRODUCTION

Vital vitamins like L-ascorbic acid (AA) possess crucial physiological functions in the human body; hence, their determination is significant for human health (1). AA with various

concentrations acts as a neuromodulator and antioxidant in the body, to measure oxidative stress levels in the human's body metabolism (2). Moreover, human, fish, birds, and mammals have to obtain their necessary AA from nature and

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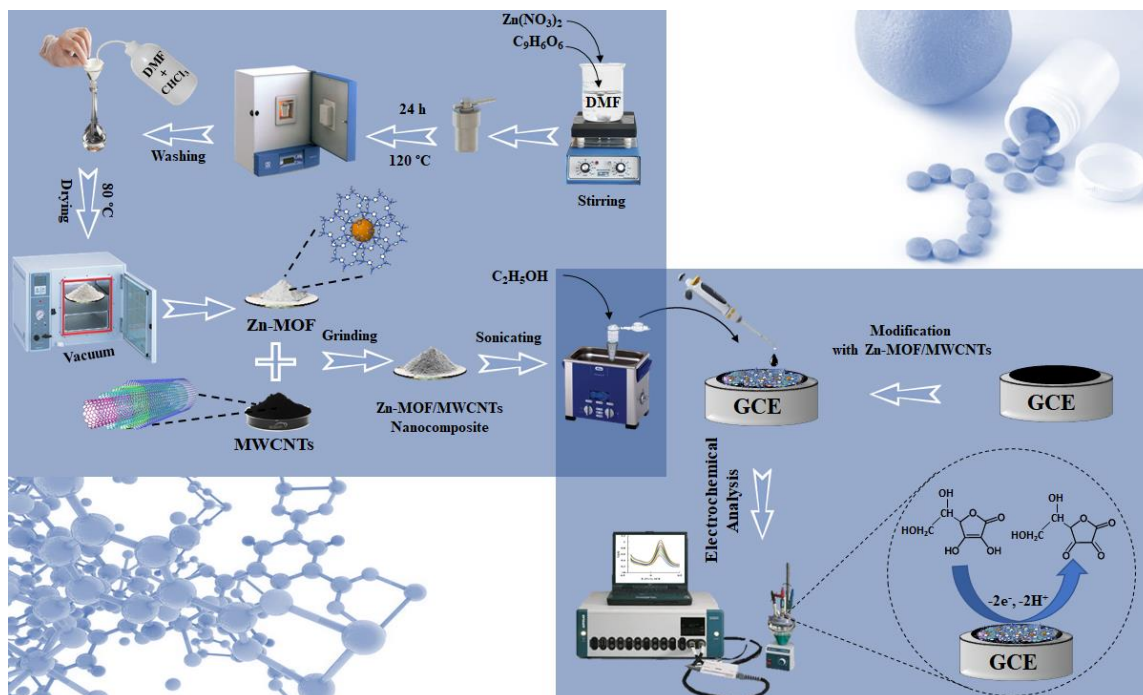
supplements due to their genetic inability to produce AA (3). The slight levels of AA in the body have been reported because of drug and alcohol abuse, disease, aging, and poor diet, which affects immune defense and the metabolic activity (4).

Several analytical approaches are used to determine AA include spectroscopy methods (Fluorescence (5), Spectrophotometry (6), UV-Vis (7), Tandem mass spectrometry (8)), High-Performance Liquid Chromatography (HPLC) (9) and Gas Chromatography (GC) (10)), electrophoresis (11), and electrochemical techniques (12). However, most of the mentioned analytical processes are costly and complicated, have low sensitivity, and require trained experts. They can also be time-consuming due to the longer preparation of samples, which requires laboratory equipment (13, 14).

Among the various analytical methods, the rapid response and convenience of electrochemical sensing with low cost and high sensitivity make it suitable for AA determination. However, sensing materials have some limitations in the electrochemical sensing systems such as weak chemical design capabilities and low surface areas. Hence, the synthesis of well-defined materials with porous structures to enhance electrochemical efficiency has considerable significance (15). Nanomaterials as useful electrode modifiers have an essential role in designing affordable, sensitive, and selective electrochemical sensors (16). The electrode modification is a significant method to improve its surface properties and have interaction with media, which consequently increases the selectivity and sensitivity of the target species (17). Metal-organic frameworks (MOFs) have several advantages, including proper stability, adaptive characteristics, large surface area, and adjustable structure (18). Moreover, MOFs can interact with analytes through van der Waals interactions, open metal sites, functional groups, and π - π interactions which make them excellent electrode modifiers (19-25). Zn (II) is one of the common cations used in the MOF fabrication; different coordination

geometries varying from four- to six-fold polyhedral can be formed owing to its electronic configuration resulting in the production of diverse secondary building units as discrete clusters or infinite rod-like structures with large inner volume (26). On the other hand, conducting polymers (27), carbon nanotubes (CNTs) (28), graphene oxide (29), and metal oxide nanoparticles (30) have been used to development of the electrochemical platforms which are effectively used for quick and efficient determination of diverse analytes like AA in various real samples with high selectivity and sensitivity. Multi-walled carbon nanotubes (MWCNTs) are also applied as electrode modifiers owing to their electrical, mechanical, and structural properties (17, 31). Despite the excellent potential of MOFs to modify various electrodes, the straight application of MOFs as electrode modifiers has been underexplored due to poor redox activity and weak conductivity. To improve the conductivity, CNTs can be combined with MOF-based compounds to form nanocomposites with higher conductivity, large surface area and mechanical strength (32).

In this research work, a metal-organic framework based on zinc (Zn-MOF) was synthesized and combined with multi-walled carbon nanotubes (MWCNTs) as a suitable modifier agent for determining of AA in human plasma samples. Initially, the glassy carbon electrode modified with the fabricated Zn-MOF/MWCNTs and the obtained electrode was investigated by various electrochemical methods including cyclic voltammetry and differential pulse voltammetry approaches. The obtained results show appropriate analytical properties including a low limit of detection (LOD) and wide linear range in the AA determination as well as suitable repeatability and reproducibility of the developed sensing assay. Eventually, the application of the proposed assay has been confirmed by the AA estimation in human plasma sample. The graphical representation of the synthesis and preparation of the desired modifier and the method of GCE electrode modification for the determination of ascorbic acid is presented clearly in Scheme 1.



Scheme 1. Schematic representation of the developed electrochemical assay for the sensitive determining of AA.

Materials and Apparatuses

All materials (such as Zinc nitrate hexahydrate, Benzene-1, 4-dicarboxylic acid, Dimethylformamide solution (DMF), Chloroform, MWCNT, Ascorbic acid, NaOH, HCl, K_2HPO_4 , H_3BO_3 , H_3PO_4 , CH_3COOH , KCl, NaCl, $NaNO_3$, $K_4[Fe(CN)_6]$) with analytical grade (Merck) were commercially available and applied without more purification. The doubled distilled water was utilized for preparing the solutions. Electrochemical experiments and techniques were performed by Autolab system (Eco Chemie B.V. model PGSTAT 12). A Shimadzo digital balance (model AEL-200) was used to weigh samples and a pH meter with an electrode of glass membrane (Metrohm, Netherlands) was employed. X-Ray Diffraction (XRD) was used to identify crystalline structure of the samples using a Tongda (TD-3700, China) and $Cu K\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) over 2θ interval 10° - 60° . The surface morphology of samples was obtained by Energy-dispersive X-ray spectroscopy (EDX) and Field Emission Scanning Electron Microscopy (FESEM) with a Tescan instrument. Fourier Transform Infrared (FT-IR) of the samples was recorded at 25°C applying a Bruker Spectrometer (model TENSOR 27, USA). All electrochemical runs were performed using a three-electrode configuration, the electrodes were purchased from Azar Electrode Company (Urmia-Iran), by applying the modified glassy carbon electrode (Zn-MOF/MWCNTs/GCE), saturated calomel electrode, and platinum electrode as

working, reference, and counter electrodes respectively.

Synthesis rout of Zn-MOF and preparation of Zn-MOF/MWCNTs nanocomposite

Zn-MOF was synthesized by solvothermal method in which zinc nitrate hexahydrate (5.2 g) with benzene-1, 4-dicarboxylic acid (1.0 g) were dissolved in 35 mL of a dimethylformamide solution (DMF, 35 mL). Next, the resulting mix was applied in a solvothermal procedure at 120°C for a day. The resulting product was rinsed with dimethylformamide solution and chloroform and finally, dried under vacuum at 80°C . Commercially-available MWCNTs (Merck) were applied to prepare the Zn-based MOF/MWCNT nanocomposite, 50 mg of MWCNTs were mixed with 5 mg of Zn-MOF through the grinding method. Then, 1 mL of ethanol was added to the prepared combination of Zn-MOF/MWCNTs and sonicated for 30 min. After preparing this suspension, it was used as a useful GCE modifier agent through developing electrochemical sensing platform.

RESULTS AND DISCUSSION

Modifier agent characterization

The XRD method presents wide information about the crystal structures and compositions of the chemical compounds. In this study, XRD was utilized to analyze the crystallinity and purity of the Zn-MOF material. The XRD pattern (Fig. S1-A) shows the existence of Zn particles. In addition, the

sharp and high peaks indicate the crystalline nature of the material under consideration (JCPDS card No. 01-080-0075). This also provides information about the coordination of the metal with the ligands to form the complex. Also, the peaks located at lower 2θ demonstrated that metal-organic frameworks have cubic crystal structures in nature (33, 34). On the other hand, in the FT-IR spectrum obtained for the Zn-MOF, the absorption bands observed at 1604 cm^{-1} correspond to the asymmetric stretching of COO^- groups, and the bands at 1467 cm^{-1} are ascribed to the symmetric stretching of COO^- groups. Also, the absorption of COO^- groups is also observed at 1658 cm^{-1} . BDC out-of-plane vibrational bands are observed at $547\text{-}1163\text{ cm}^{-1}$ and the corresponding vibration of the benzene base can be shown at 1820 cm^{-1} (Fig. S1-B).

It can be seen from the EDX images that the major fraction of elements in Zn-MOF are C, O, and Zn with 69.11%, 22.22%, and 8.67%, respectively (Fig. S1-C), revealing that there are no impurities in the MOF structure. Finally, the morphology of Zn-

MOF was investigated by FESEM and its crystalline structure was confirmed (Fig. S1-D) and also dot-mapping of C, O and Zn for the Zn-MOF is shown in Fig. S1(E-H).

Electrochemical behavior of AA by applying the developed sensing assay

To study the electrochemical behavior of the Zn-MOF/MWCNTs/GCE toward AA, cyclic voltammetry was first recorded at the bare GCE in a solution containing 1 mL AA (2 mM) and 9 mL phosphate buffer (0.1 M, pH= 7) with KCl (0.1 M) as the supporting electrolyte ($\nu= 50\text{ mV/s}$). After modification of the GCE with Zn-MOF, the oxidation peak potential and current were observed at 0.235 V and $6\text{ }\mu\text{A}$, respectively. Upon further modification with Zn-MOF/MWCNTs, the peak potential shifted negatively to 0.187 V, revealing enhanced electrocatalytic activity, while the peak current increased to $7.45\text{ }\mu\text{A}$, indicating an increase in the electroactive surface area. The corresponding results are presented in Fig. 1-A and 1-B.

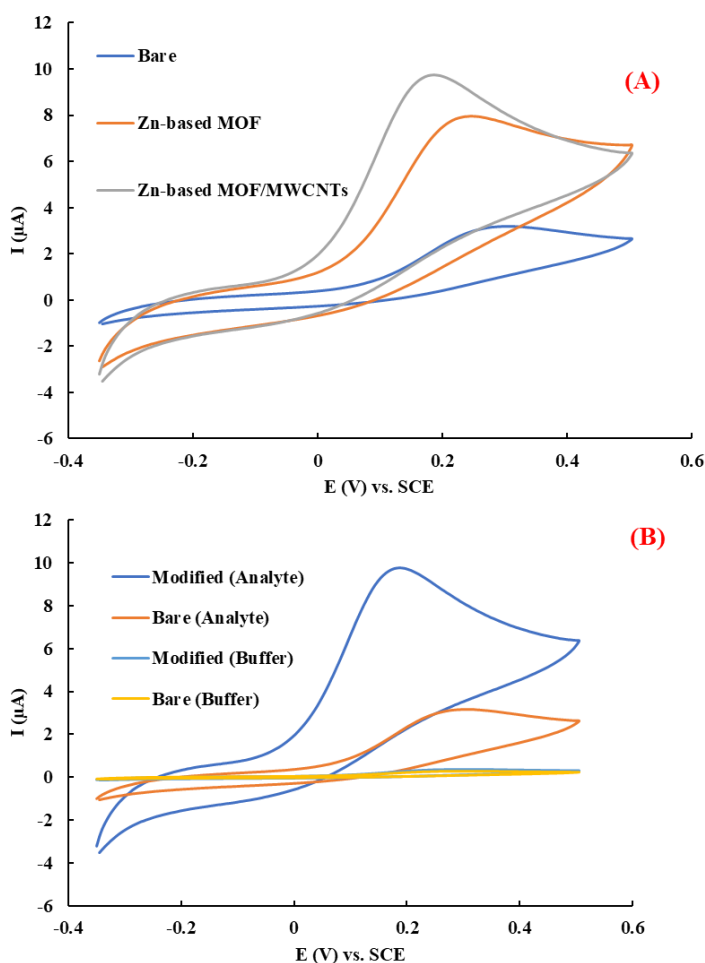


Fig. 1. Electrochemical performance of ascorbic acid on Zn-MOF/MWCNTs/GCE electrodes (A and B).

Investigation of the optimized conditions in performance of the designed sensor

Modifier volume

Electrochemical responses can be remarkably affected by the volume of the modifying agent. Accordingly, different volumes of 1-5 μL of the prepared nanocomposite in the ethanol were immobilized on the GCE surface and the electrochemical behavior of the modified electrode was studied in the AA solution (0.2 mM) by applying the CV method ($E = -0.4 - 0.6$, and $v = 50$ mV/s). Therefore, the drop volume of 3 μL was chosen as the optimal amount owing to more AA oxidation, resulting in a higher anodic peak (Fig. 2-A and B).

Buffer type and concentration

Phosphate and Britton-Robinson (BR) solutions (0.1 M, pH=7) were employed to study the efficacy

of the buffer type. The CVs of AA (0.2 mM) using the designed electrode were recorded in each buffer. As a result, the higher current for AA was observed in the phosphate buffer (Fig. 2-C and D). Likewise, the effect of phosphate buffer concentration (0.01-0.2 M) at pH=7 on the voltammograms was investigated and the outcomes are indicated in Fig. 2-E and F. Consequently, 0.1 M of phosphate buffer was chosen as the optimal concentration.

The supporting electrolyte type and concentration

Three supporting electrolytes including NaNO_3 , KCl, and NaCl at a concentration of 0.1 M, were prepared in phosphate buffer (0.1 M, pH=7), to study the effect of the electrolyte type. As a results, KCl was chosen as the appropriate supporting electrolyte with the optimal concentration of 0.1 M (Fig. 2G -J).

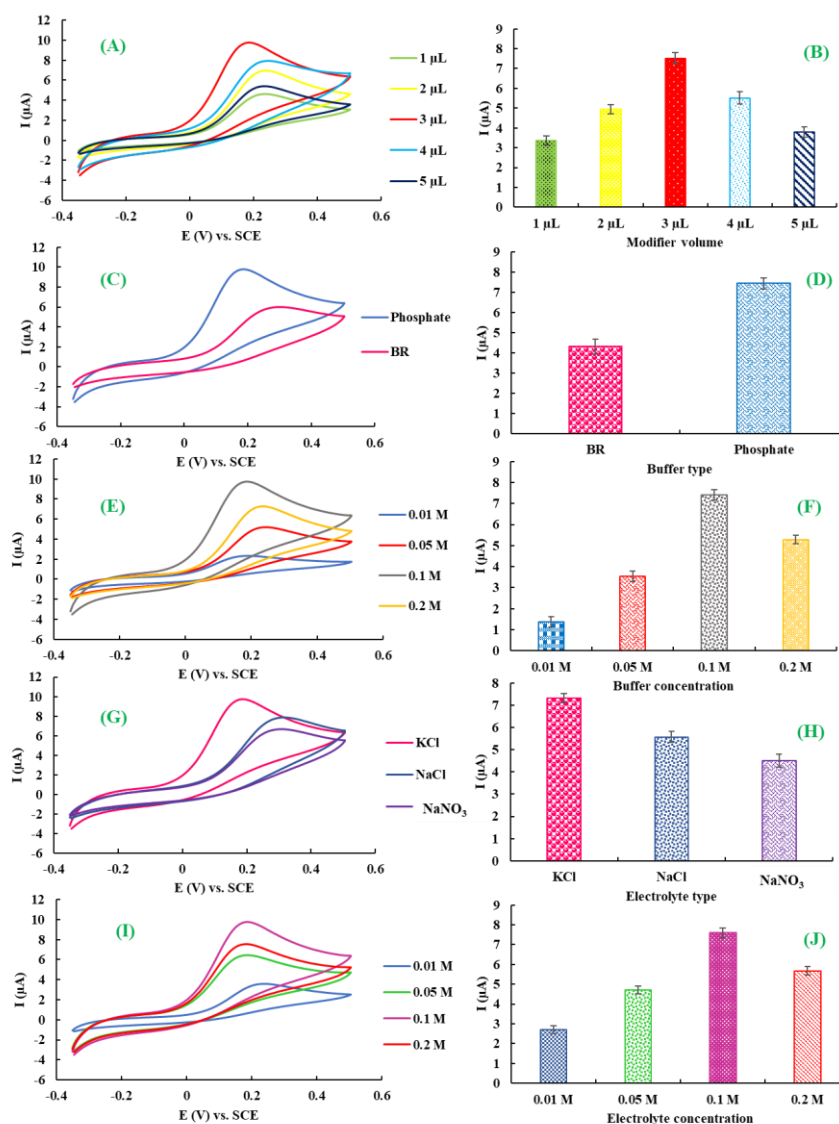


Fig. 2. Optimization of the experimental parameters with corresponding histograms illustrating the effects of modifier volume (A and B), buffer type (C and D), buffer concentration (E and F), supporting electrolyte type (G and H), and supporting electrolyte concentration (I and J).

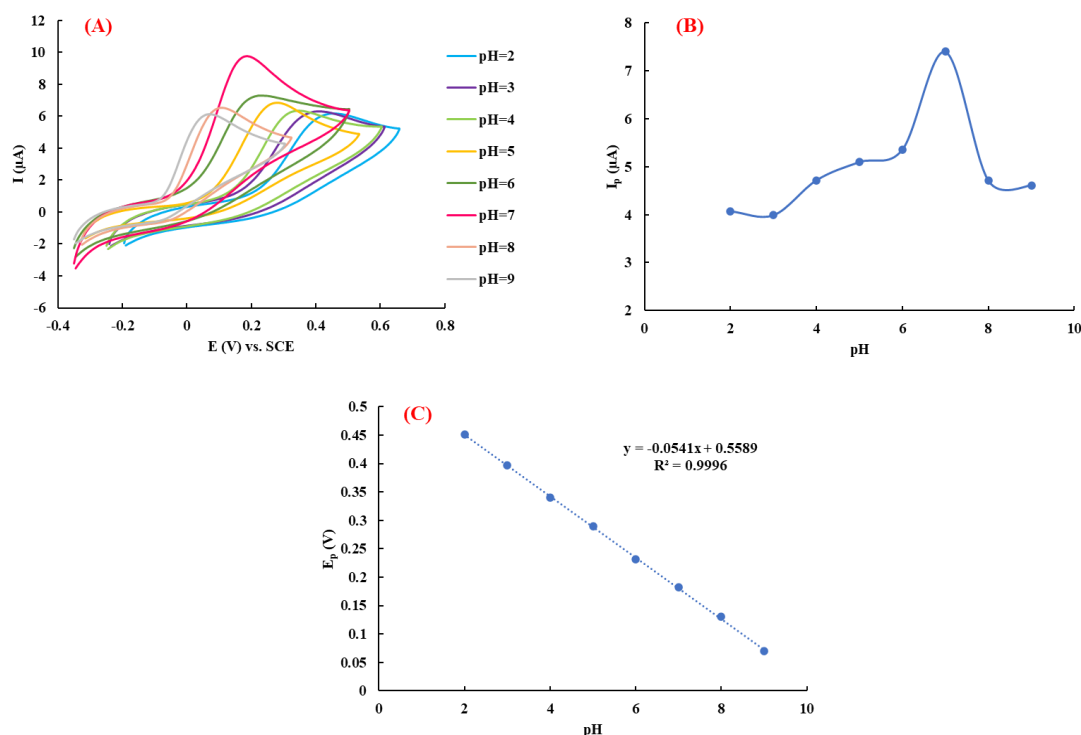


Fig. 3. (A) Investigation of the pH effect, (B) Dependency of I_p vs. pH, and (C) Dependency of E_p vs. pH.

pH Investigation

To study the efficacy of pH, buffer solutions (pH= 2-9) were prepared in the presence of AA, and the related cyclic voltammograms were recorded. According to Fig. 3-A, pH=7 was chosen as the optimal value. The relationship between I_p and pH is demonstrated in Fig. 3-B. Furthermore, Fig. 3-C depicts the linear relationship between the E_p and pH amounts in which by increasing the solution pH, E_p shifts to less positive potentials. The obtained results clearly demonstrate the involvement of proton transfer in the AA oxidation process. The plot slope is -0.0541, near the slope of Nernst plot, indicating that the electrons are equal to the protons.

Kinetics study

To study the efficacy of the scan rate, several scan rates ($v = 10$ -300 mV/s) were investigated, and the cyclic voltammograms were recorded as well (Fig. 4-A). The peak height of the voltammogram increased with increasing the scan rate by applying the modified electrode; when diffusion phenomena control the electrochemical process, the I_p is linearly proportional to the $v^{1/2}$. On the other hand, if it is controlled by a non-diffuse phenomenon, I_p is linearly correlated to v . To realize the

electrochemical mechanism, the comparison of Fig. 4-B and C reveals that I_p dependency of AA versus $v^{1/2}$ is more linear than its dependency on v . Thus, the electrochemical procedure is controlled by the AA diffusion phenomenon from the solution to the surface of the electrode. Besides, according to the Fig. 4-D, the diffusion mechanism of AA is also confirmed by the slope close to 0.5.

Evaluation of the electron numbers

As shown, the excess potential for AA oxidation increases and shifts to more positive amounts when the scan rate is enhanced. This can be ascribed to the limitation of kinetic in the process of electrode. Consequently, according to the Tafel equation (Eq. (1) and also Fig. 4-E), it is essential to estimate the electrons transferred in the rate-determining step; the electron numbers are determined using the slope of $\log I$ against the potential at the lower scan rates.

$$\log I = \log I_0 + \frac{(1-\alpha)n_a}{0.059} \eta \quad (1)$$

In general, the slow step of an electrochemical reaction involves one electron; hence, n_a is considered as 1, and α is calculated.

$$\frac{(1-\alpha)n_a}{0.059} = 8.504, (1-\alpha)n_a = 0.501, \alpha = 0.498$$

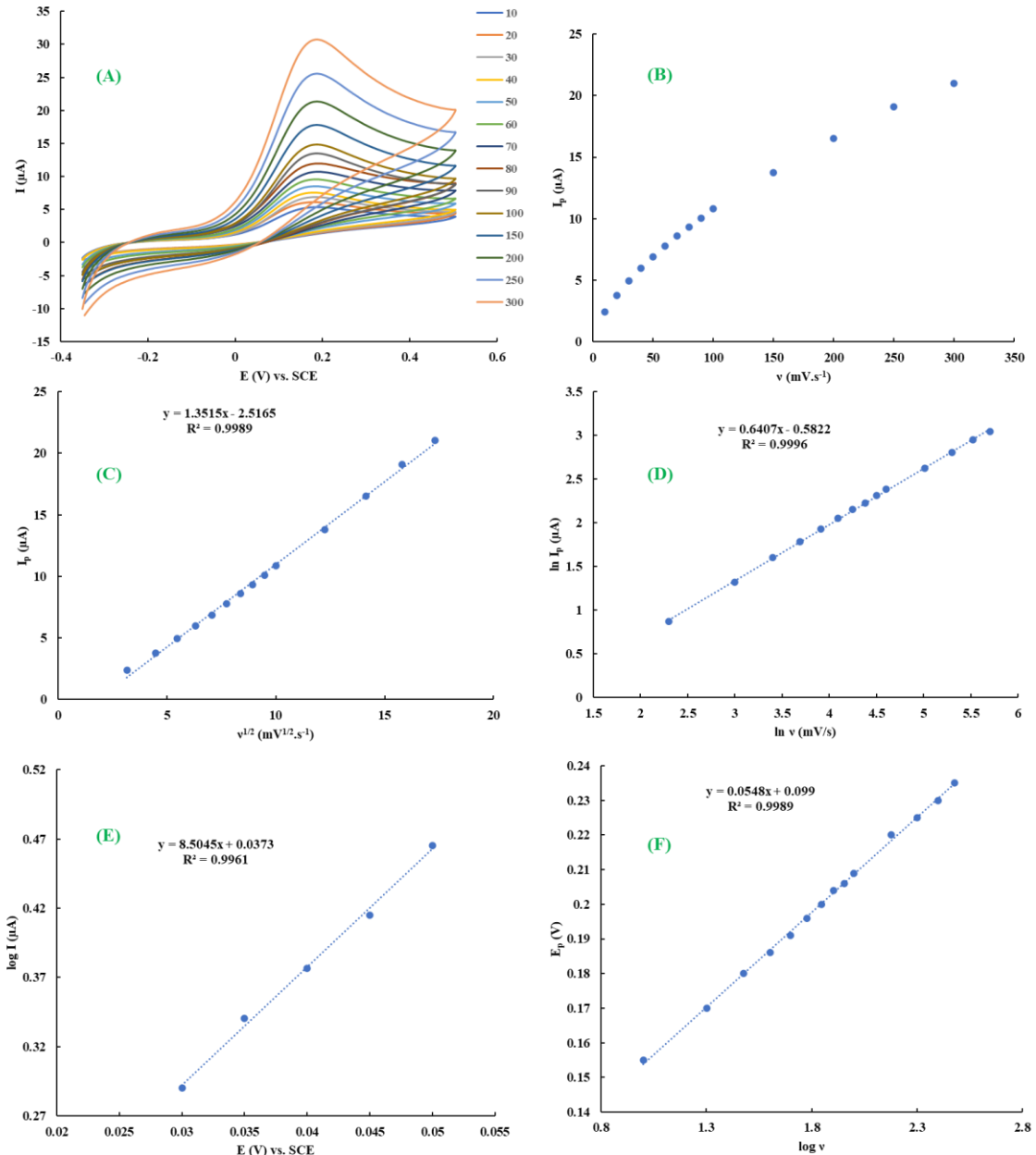


Fig. 4. (A) Voltammograms recorded using the electrode after modification, (B) Dependency of I_p vs. v , (C) Relation between variations in anodic peak currents based on the square root of the scan rate, (D) Plot of $\ln I_p$ against $\ln v$, (E) logarithmic current changes in the terms of potential, and (F) Changes of the E_p in relation to the $\log v$.

By the way, n_a can be calculated by the Tafel slope $[(1 - \alpha)n_a / 0.059]$. Moreover, the Laviron equation (Eq. (2)) demonstrates the dependency of the peak potential and the $\log v$ in a diffusion-controlled irreversible process, also, K is a constant value and b is the Tafel slope.

$$E_p = \left(\frac{b}{2}\right) \log v + K \quad (2)$$

Fig. 4-F was depicted based on Eq.2 for the AA oxidation. n_a calculated by the obtained slope as follows:

$$b = 2 \times 0.0548 = 0.109$$

$$b = \frac{2.3 RT}{(1 - \alpha)n_a F} = \frac{0.059}{(1 - \alpha)n_a}$$

$$(1 - \alpha)n_a = \frac{0.059}{0.109} = 0.538 \quad \alpha = 0.498 \quad n_a = 1.098 \approx 1$$

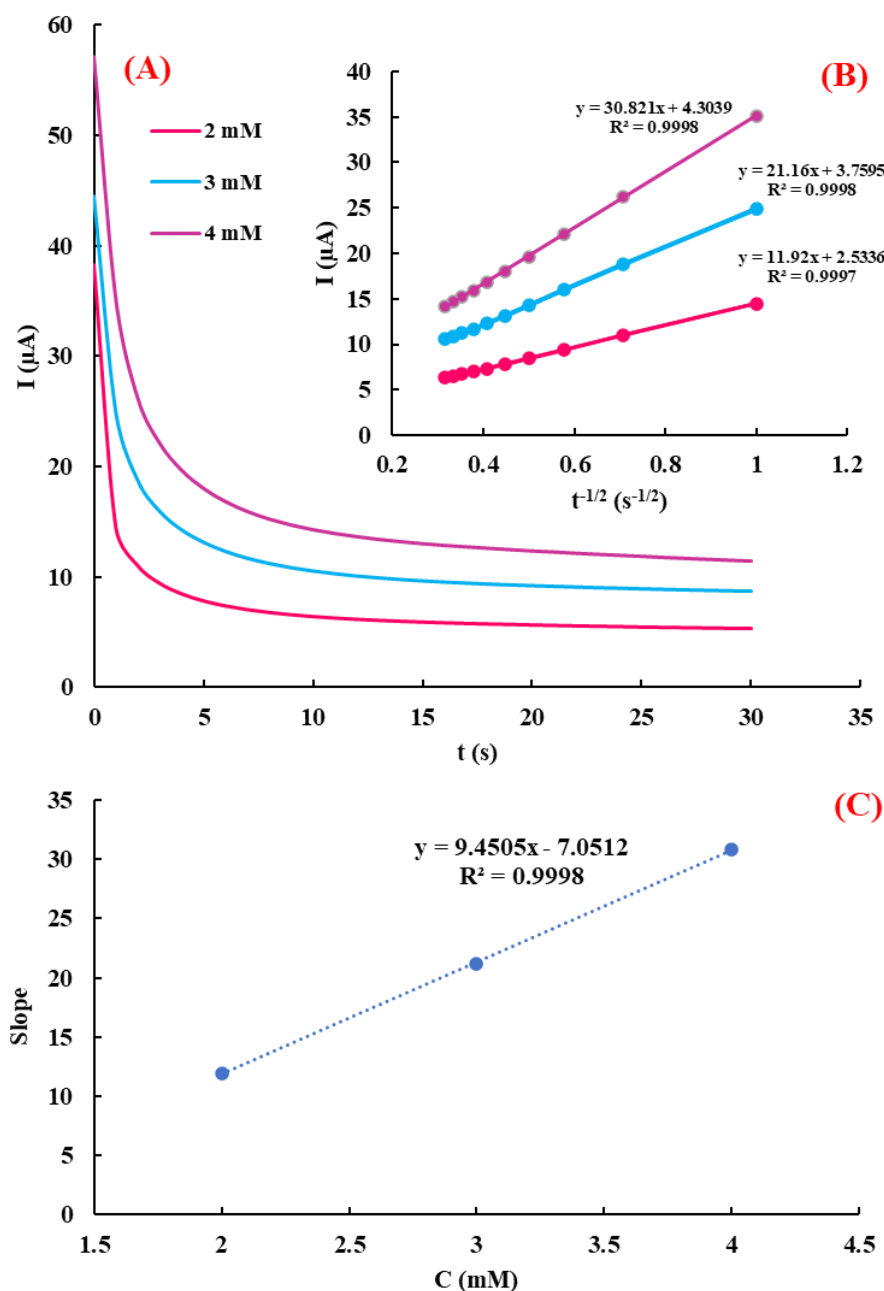


Fig. 5. (A) Chronoamperograms of Zn-MOF/MWCNTs/GCE, (B) The plots related to the current regarding the inverse of the square of time, (C) The slope of the lines ($I-t^{-1/2}$) based on the concentration of ascorbic acid.

Investigating the effective surface area of the electrode

To investigate the effective surface area of the electrode, the bare electrode, the Zn-MOF modified electrode, and the Zn-MOF/MWCNT modified electrode were evaluated in 0.1 M $[\text{Fe}(\text{CN})_6]^{3-/4-}$. The surface areas were obtained 0.016, 0.042, and 0.093 cm^2 , respectively. The results indicate a multi-fold increase in the surface area of the modified electrodes compared to the bare electrode (Fig. S2. A-F).

Evaluation of the electro-catalytic oxidation of AA using the Chronoamperometry method

Considerable data about how a substance is transmitted to an electroactive surface and the main effective variables connected to its diffusion can be provided by chronoamperometric studies. For this purpose, various solutions of AA (concentration range of 2–4 mM) were prepared to evaluate the AA diffusion coefficient in the oxidation process. The chronoamperograms of AA solutions were recorded by applying 0.4 V for 30 s (Fig. 5-A). Afterward, the diagram of the current intensity against $t^{-1/2}$ was plotted for each

Chronoamperometry (Fig. 5-B). Based on the Cutterell equation (Eq. (3)) and according to the Fig. 5-C, the slope of each line is demonstrated versus the analyte concentration, a line was observed with a slope of $nFAD^{1/2}/\pi^{1/2}t^{1/2}$.

$$I = nFACD^{1/2}/\pi^{1/2}t^{1/2} \quad (3)$$

By replacing the amounts of I (current intensity in coulomb per second), t (time in seconds), F (Faraday number in coulomb per volt), n (number of transferred electrons), C (electro-active compound (ascorbic acid) concentration in mol/cm³), A (the electrode area in cm²), and the diffusion coefficient (D) was calculated as 3.011×10^{-6} cm²/s (35).

Study of the analytical features of the designed assay

DPV approach with high sensitivity can be applied effectively in the electrochemical analysis. DP-voltammograms demonstrate that, with increasing AA concentration, the peak potential (E_p) remains constant while the peak current (I_p) increases (Fig. 6-A). The calibration plot is linear in the concentration range of 2-22 μ M, which can be applied to evaluate the detection limit. The limit of detection (Y_{LOD}) is a parameter equal to the analyte concentration with a device response, which differs

meaningfully from the response for the white sample (Y_B). It can be estimated by the following accepted relationship in which S_B is the standard deviation of the white sample (Eq. (4)). This equation is also applied to determine the unknown sample concentration.

$$Y_{LOD} = Y_B + 3S_B \quad (4)$$

The intercept of this equation is considered a suitable estimation for Y_B . The S_B calculation is time-consuming and difficult in practice because it needs several repeated experiments for the white sample solution. As a result, the statistical parameter of $S_{y/x}$ is applied instead of using the following equation (Eq. (5)):

$$S_{y/x} = \sqrt{\frac{\sum_i (y_i - \hat{y}_i)^2}{n-2}} \quad (5)$$

y_i is the calculated value of the response of the device which was evaluated by replacing the concentration amount in the line equation and n is the points of the calibration plot (Fig. 6-B). Moreover, Y_{LOD} is determined using the obtained $S_{y/x}$ and a (Eq. (5)) from the DPV results as 1.21 μ M. The effective comparison of the developed sensing assay with other similar approaches is demonstrated in Table 1.

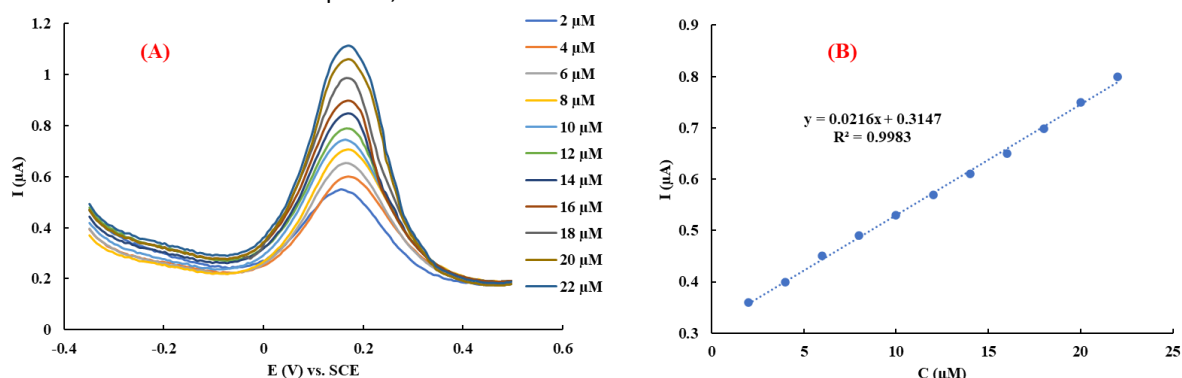


Fig. 6. (A) DPVs of Zn-MOF/MWCNTs/GCE for ascorbic acid, (B) Calibration plot.

Table 1. Analytical comparison of the desired sensing assay with other developed platforms used to determine ascorbic acid.

Electrochemical method	Modifier	LOD (μ M)	Reference
CV and DPV	C ₃ N ₄ /MWNTs/GO ² hybrid	96	(3)
CV and LSV ¹	r-GO/NPs ³	5.63	(36)
CV, DPV and SWV ⁴	Polyaniline	5.1	(15)
CV and DPV	2D-titanium carbide (MXene)	4.6	(37)
CV and DPV	Zn-MOF/MWCNTs	1.21	This research work

1) Linear Sweep Voltammetry ; 2) Graphene Oxide ; 3) Reduce Graphene Oxide/Nanoparticles ; 4) Square Wave Voltammetry

Table 2. Determination of ascorbic acid in human plasma sample (n=3).

Human Plasma Sample	Added Concentration (nmol)	Founded Concentration (nmol)	Mean (nmol)	Recovery (%)	RSD (%)
1	100	91.2 93.1 95.0	93.1	93.1	2.04

Repeatability, reproducibility, and stability

In order to investigate the repeatability, CVs of AA were recorded five times using the same modified electrode. On the other hand, the CV tests were efficiently performed for determination of AA with five different electrodes to evaluate the reproducibility. To examine the electrode stability, 100 runs of the cyclic voltammetry were carried out, and 1, 20, 40, 60, and 100 cycles were selected. As a result, similar current intensities were observed. The relative standard deviation (RSD) percentages in all above-mentioned steps were lower than 5%, which clearly demonstrates the efficient precision of the developed electrode for the AA determination from a practical viewpoint.

Investigating the effect of interfering agent

To study the effect of interfere in the determination of ascorbic acid, the related DPVs were effectively recorded in the presence of piroxicam as an interfering agent. Then the calibration plot was recorded for ascorbic acid in the presence of piroxicam. Accordingly, it is possible to measure ascorbic acid in the presence of the mentioned interfering agent. The slope obtained from the calibration plot for ascorbic acid in the presence of interfering factor is approximately near to the slope of the calibration plot for ascorbic acid in the absence of interfering agent (Fig. S3-A and B).

AA determination in human plasma sample

To investigate the accuracy of the developed sensor for AA determination, the method of standard addition was effectively applied by spiking different concentrations of the AA standard solution (2 mM) in human plasma sample. Consequently, recovery index was found equal to 93.1% with RSD of 2.04 (Table 2), representing the appropriateness of the designed electrochemical assay for the determination of AA in biological complex matrices.

CONCLUSIONS

L-ascorbic acid (AA) is an important biological compound due to its physiological roles as an antioxidant and neuromodulator, and its reliable determination in biological matrices remains analytically significant. In this work, a Zn-MOF/MWCNTs nanocomposite-modified glassy carbon electrode was fabricated and evaluated as an electrochemical sensing platform for AA determination.

The modification of the GCE with Zn-MOF/MWCNTs led to an improved electrochemical

response toward AA, which can be attributed to the enhanced electrode surface characteristics and facilitated electron transfer at the electrode-solution interface. Under the optimized experimental conditions, the proposed sensor exhibited a linear response in the concentration range of 2–22 μM with a detection limit of 1.21 μM . The analytical performance of the developed electrode was further assessed in terms of repeatability, reproducibility, and operational stability, showing acceptable results for electrochemical measurements. In addition, the applicability of the proposed method was examined by determining AA in human plasma samples, resulting in a recovery of 93.1%, which demonstrates the feasibility of the sensor in a complex biological matrix.

In conclusion, the Zn-MOF/MWCNTs-modified GCE provides a simple and effective electrochemical approach for AA determination. While the method shows satisfactory analytical performance and practical applicability, it may serve as a basis for further optimization and development of MOF-based electrochemical sensors for biological analysis.

AUTHORS' CONTRIBUTION

S.Jalali: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Visualization, Writing-original draft, Writing-review and editing.

J.Abolhasani: Conceptualization, Data curation, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing-original draft, Writing-review and editing.

H.Sohrabi: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing-original draft, Writing-review and editing.

S.Ershad: Resources, Supervision, Validation, Visualization, Writing-original draft, Writing-review and editing.

B.Vahid: Formal analysis, Validation, Visualization, Writing-original draft, Writing-review and editing.

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ETHICAL STATEMENT

Not applicable.

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