

Article

Synergistically Enhanced Electrochemical Sensing of Food Adulterant in Milk Sample at Erbium Vanadate/Graphitic Carbon Nitride Composite

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Abstract: Dimetridazole (DMZ), a nitroimidazole derivative, is a notable antibiotic that has garnered growing interest in the medical community owing to its noteworthy pharmacological and toxicological properties. Increasing interest is being directed toward developing high-performance sensors for continuous monitoring of DMZ in food samples. This research investigated an electrochemical sensor-based nano-sized ErVO_4 attached to a sheet-like g-CN-coated glassy carbon electrode to determine dimetridazole (DMZ). The chemical structure and morphological characterization of synthesized $\text{ErVO}_4/\text{g-CN}$ were analyzed with XRD, FTIR, TEM, and EDS. Irregular shapes of ErVO_4 nanoparticles are approximately 15 nm. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were followed to examine the electrochemical performance in pH 7 phosphate buffer solution for higher performance. This electrochemical sensor showed a low detection limit (LOD) of 1 nM over a wide linear range of 0.5 to 863.5 μM . Also, selectivity, stability, repeatability, and reproducibility studies were investigated. Furthermore, this electrochemical sensor was applied to real-time milk sample analysis for the detection of analytes.

Keywords: ErVO_4 ; g- C_3N_4 ; composite; electrochemical detection; dimetridazole

Citation: Sanjeevani, U.G.A.; Wang, S.-F. Synergistically Enhanced Electrochemical Sensing of Food Adulterant in Milk Sample at Erbium Vanadate/Graphitic Carbon Nitride Composite. *Sensors* **2024**, *24*, 1808. <https://doi.org/10.3390/s24061808>

Academic Editor: Weiying Lu

Received: 25 January 2024

Revised: 29 February 2024

Accepted: 5 March 2024

Published: 11 March 2024



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1. Introduction

1,2-Dimethyl-5-nitro imidazole (dimetridazole or dimet or DMZ) is a nitroimidazole-type veterinary drug used for bacterial and protozoal infections in animals, and it is used as a growth promoter in meat production to enhance efficiency in feeding. DMZ is banned in food processing in many countries because the residue of DMZ leads to mutagenicity, carcinogenicity, and genotoxicity in the human body. While the United States, Canada, Japan, and China have already banned DMZ, the United States and the European Union have also established a maximum residue limit of biological samples such as meat and milk. Among different biological matrices, milk has a lower maximum residue limit, and the detection limit is required to be $\leq 2 \mu\text{g/kg}$ [1–5].

DMZ can be determined by electrochemical methods, immunoassay, thin-layer chromatography (TLC), gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC), and liquid chromatography–mass spectrometry (LC–MS). Among these methods, GC and GC–MS need derivatized analytes, and HPLC needs a large sample volume, a long elution time, and is of high cost [6,7]. Because of these drawbacks in chromatography methods, the electrochemical method with a low detection limit becomes compatible with detecting DMZ in different environments. The advantages of electrochemical methods are low cost, high sensitivity, and detection of a wide range of target analytes. Cyclic voltammetry is a successive electrochemical method to analyze the oxidation and reduction reaction of a substance [8]. Coating nanomaterials can increase sensitivity, absorption, adsorption, and efficiency of

application. Large specific surface areas of nanomaterials help to develop better limits of detection (LOD) and sensitivity [9].

Oxide-based materials are frequently used in electrochemical applications. Rare earth elements have gotten more attention in recent years because rare earth oxides are used in photocatalysis, thin film phosphors, and magnetics technologies. Among these oxides is rare earth orthovanadate (RVO_4), which has unique chemical and physical properties. Moreover, rare earth orthovanadate structure exists in monoclinic monazite-type and a tetragonal zircon-type polymorphous compounds [10]. Erbium (Er) is the 11th atom of REE, attracting attention in recent doping photocatalyst applications [11]. Vanadium has oxidation states of +5, +4, +3, and +2 [12]. Diverse oxidation numbers of vanadium can be mixed with varied chemical elements, opening access to use in many applications. The study of the electrocatalytic behavior of erbium vanadate (ErVO_4) is promising due to the compound's high stability and excellent repeatability value. Moreover, RVO_4 ; $\text{R} = \text{La, Ce, Nd, Sm, Eu, and Gd}$ are the frequently used elements in electrochemical sensor applications and there are fewer electrochemical studies have been reported on ErVO_4 [13,14].

Hydrothermal, solvothermal, sol-gel, Pechini, co-precipitation, and ion exchange methods can synthesize nano-sized materials. Furthermore, chemical methods have more advantages than mechanical methods. Even high-temperature methods are available, but some nanomaterials are unstable at elevated temperatures, which is a disadvantage for commercial usage [15,16]. The hydrothermal method uses a temperature range of 60–200 °C and controls the nucleation and crystal growth of RVO_4 . Therefore, effective nano-sized powder with a high surface area of ErVO_4 can be easily prepared from the hydrothermal method for sensor application; catalytic performance depends on particle size and surface area [17–19].

Carbon-based materials are widely studied due to the advantages of structural chemical properties and electrical characteristics. Many researchers have proven that doping heteroatoms, such as nitrogen, sulfur, boron, and iodine, with carbon can enhance electrochemical performance. Among previously mentioned heteroatoms, nitrogen attached to carbon studies show excellent catalytic activity. Graphitic nitride-based nanocomposites are low cost, have low toxicity, are highly thermal durable, and can be applied in photocatalytic applications, biomedical applications, and hydrogen generation for the reasons mentioned previously. Thermal treatment with melamine, dicyanamide, and cyanamide can be applied in order to synthesize g-CN; melamine is prominent for having a large g-CN surface area. High electrical conductivity due to a lone pair of nitrogen atoms attached to carbon band gap of ~2.7 eV is beneficial to electrochemical sensor usage as carbon support with ErVO_4 . Furthermore, the overall detecting properties are improved by molecular-level interactions and size confinement effects as a result of the improved synergistic effects between g-CN and ErVO_4 as well as the significantly altered active surface area of the ErVO_4 @g-CN nanocomposite [20–31].

In this research work, erbium vanadate attached to a graphitic carbon (ErVO_4 @g-CN) heterostructure was prepared by sonication, and optimization for the electrochemical detection of DMZ was carried out. The proposed ErVO_4 @g-CN/GCE-modified electrode enhanced the electrochemical behaviors on DMZ determination with a wide linear range and low detection limit. Furthermore, the ErVO_4 @g-CN/GCE-modified electrode revealed good selectivity, stability, repeatability, and reproducibility with a less than $\pm 5\%$ relative standard deviation. Furthermore, the practicability of the proposed sensor was applied to spiked milk samples. Finally, the above-discussed electrochemical sensor is a promising candidate for electrochemical monitoring of DMZ in real-world samples.

2. Experimental Section

2.1. Materials and Reagents

Erbium (III) nitrate pentahydrate ($\text{ErH}_{10}\text{N}_3\text{O}_{14}$), ammonium metavanadate ($\text{NH}_4\text{VO}_3 \geq 99\%$ purity), and urea ($\text{CH}_4\text{N}_2\text{O}$) were purchased from Sigma Aldrich, China and

Showa Chemical Co. Ltd., Tokyo, Japan. Potassium chloride (KCl), Potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), and Potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) were obtained from Showa Chemical Co. Ltd., Tokyo, Japan. Sodium phosphate dibasic and sodium dihydrogen phosphate (Na_2HPO_4 and NaH_2PO_4) were utilized to prepare 0.1 M (pH 7) PBS (phosphate buffer solution). All the electrochemical experiments were carried out using 0.1 M PBS (pH 7) as the supporting electrolyte. Milk samples were brought in from a nearby convenience store. These samples were centrifuged and diluted before further experiment. Prepared samples were spiked with known concentrations to use for the detection of DMZ separately.

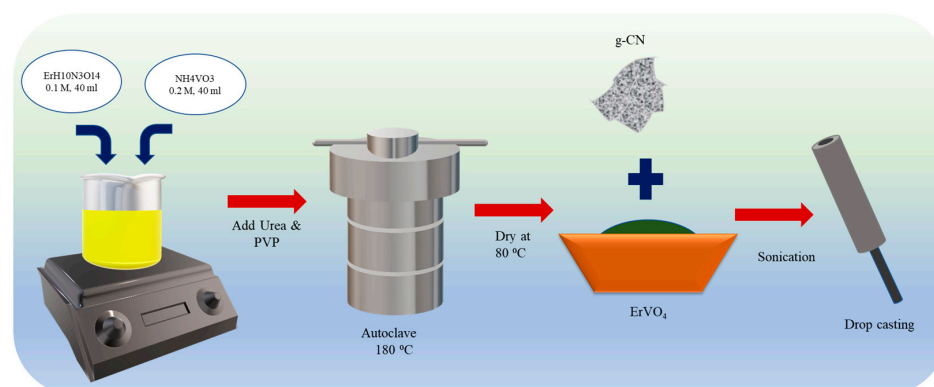
All analytical grade chemicals were used as received without further purification in these experiments. Details regarding materials characterization instruments are given in supporting information.

2.2. Instruments

XRD analysis was performed using a Bruker, Rigaku D/maxB, DMX-2200 instrument, Taiwan. The morphology and elemental mapping of sample was analyzed using a high-resolution (HR) transmission electron microscope (TEM) (JEOL JEM-2100F (HR)) operating at 200 kV and by energy-dispersive X-ray spectroscopy using EDAX AMETEK Inc., DigitalMicrograph[®] software. Fourier transform infrared spectra (FTIR) were tested using Nicolet 6700 (Thermo Fisher Scientific, USA). Electrochemical impedance spectroscopy and electrochemical measurements were carried out with Ω -metrohm auto lab (AUT51770, 100–240 V~75 VA50/60 Hz) instrument, Taiwan (Nova 2.1 software) and CHI 1211c electrochemical workstation (Taiwan). A glassy carbon electrode (surface area = 0.072 cm^2), Ag/AgCl, and a Pt wire were the working, reference, and counter electrodes, respectively in this electrochemical analysis.

2.3. Synthesis of ErVO_4

The hydrothermal process was followed in synthesizing ErVO_4 in order to obtain nanocrystalline material. Erbium (III) nitrate pentahydrate ($\text{ErH}_{10}\text{N}_3\text{O}_{14}$) and ammonium metavanadate (NH_4VO_3) were added in a stoichiometric ratio of 1:2 to the 40 mL of distilled water in a small beaker and then stirred. Next, 0.03 g of urea was added to the solution, and the resultant solution was transferred to a Teflon autoclave after 2 h of stirring and heated at 180°C for 18 h. The resultant green-colored product was centrifuged with water/ethanol and washed several times. Finally, ErVO_4 was dried at 80°C for 24 h to be used for further experiments (Scheme 1).



Scheme 1. Preparation of ErVO_4 nanoparticles.

2.4. Synthesis of Graphitic Carbon Nitride (g-CN)

The thermal treatment method was followed for preparation. A quantity of 5 g of g-CN of melamine was added to 25 mL distilled water and stirred at 90°C , and the resultant precipitate of melamine–cyanuric acid (MCA) was dried until there was no moisture in the

sample. Then, it was transferred to N₂ inserted tubular furnace, and calcined at 550 °C for 3 h. Yellow powder was collected for the preparation of a composite [32].

2.5. Preparation of ErVO₄@g-CN-Modified GCE

A composite was prepared by changing the weight ratio of ErVO₄ and g-CN in H₂O, followed by sonication for 15 min. For fabrication, the glassy carbon electrode (GCE) was polished using alumina slurry and cleaned with water/ethanol to remove contamination. Then, this well-prepared GCE was kept for drying at room temperature for further usage. The optimized composite (weight ratio of 3:1, ErVO₄: g-CN in H₂O) was coated onto the GCE using the drop-casting method, which was then kept in a laboratory oven at 60 °C for drying [33].

3. Results and Discussion

3.1. Characterization of ErVO₄@g-CN

Synthesized g-CN, ErVO₄, and ErVO₄@g-CN were analyzed with an X-ray diffractometer (XRD) as shown in Figure 1a. Peaks in the XRD spectrum of crystalline ErVO₄ exhibit diffraction patterns at 2 theta values of 25.07° as well as at values of 31.56°, 33.67°, 35.75°, 40.72°, 45.17°, 48.42°, 49.92°, 51.46°, 58.07°, 62.91°, 64.96°, 70.80°, and 74.52°, which correspond to the (200), (211), (112), (220), (202), (301), (103), (321), (312), (400), (420), (332), (204), (224), and (512) planes, respectively (JCPDS 01-072-0860). The g-CN shows an amorphous nature in XRD, which can be seen in the composite of the ErVO₄@g-CN/GCE pattern near the 2θ values of 27°. These results confirm the formation of a crystalline ErVO₄ nanocomposite.

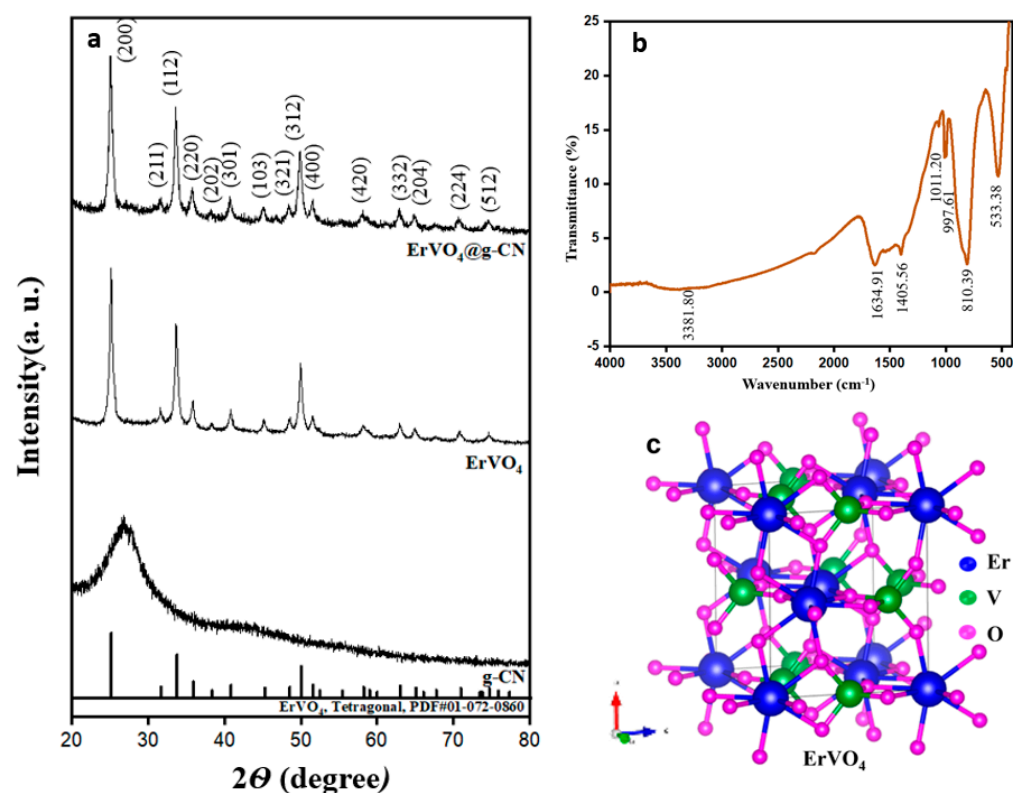


Figure 1. (a) XRD of g-CN, ErVO₄, and ErVO₄@g-CN. (b) FTIR of ErVO₄@g-CN. (c) Crystal structure of tetragonal ErVO₄.

The ErVO₄@g-CN compound was further analyzed with FTIR for bond formation details, as shown in Figure 1b. The sharp peak at 533.38 cm⁻¹ describes the Er-O stretching vibrations, and the V-O is represented by the stretching vibrations at 997.61 cm⁻¹. The peak at 1011.20 cm⁻¹ corresponds to the stretching vibration of (V=O). The peaks at

1401.56 cm^{-1} and 1634.91 cm^{-1} are due to the stretching vibrations of (C-N) and C=N in g-CN. The stretching vibrations of (N-H) in $-\text{NH}_2$ and $=\text{N}-\text{H}$ can be defined from the broad peak at 3381.80 cm^{-1} . The confirmed s-triazine ring of the bending vibration is at 810.39 cm^{-1} [34–37]. The tetragonal crystal system with a 141/amd space group of ErVO_4 is shown in Figure 1c. Er^{3+} is attached to eight equivalent O^{2-} atoms, and V^{5+} is bonded to four equivalent O^{2-} atoms.

Coral patterns, such as the nano-sized ErVO_4 -attached g-CN, can be seen in the Figure 2a FE-SEM images. A further examined ErVO_4 @g-CN microstructure from the HR-TEM images is displayed in Figure 2b,c. Nano-sized ErVO_4 can be seen on sheet-like g-CN from the HR-TEM images in Figure 2b; the lattice fringe with an interplanar spacing value of 0.32 nm corresponding to the (200) crystal plane of ErVO_4 is exhibited in Figure 2c. Also, the SAED image of Figure 2d reflects the crystal plane from the XRD analysis. The elemental distribution of compounds from the EDS analysis was studied, and this analysis further proved the presence of elements. The atomic percentages of C, N, O, V, and Er are 35.8%, 34.1%, 18.2%, 6.9%, and 5.1%, respectively, as depicted in Figure 2e. Furthermore, EDS mapping from the TEM images confirms the presence of erbium, vanadium, oxygen, carbon, and nitrogen, as shown in Figure S2a–f.

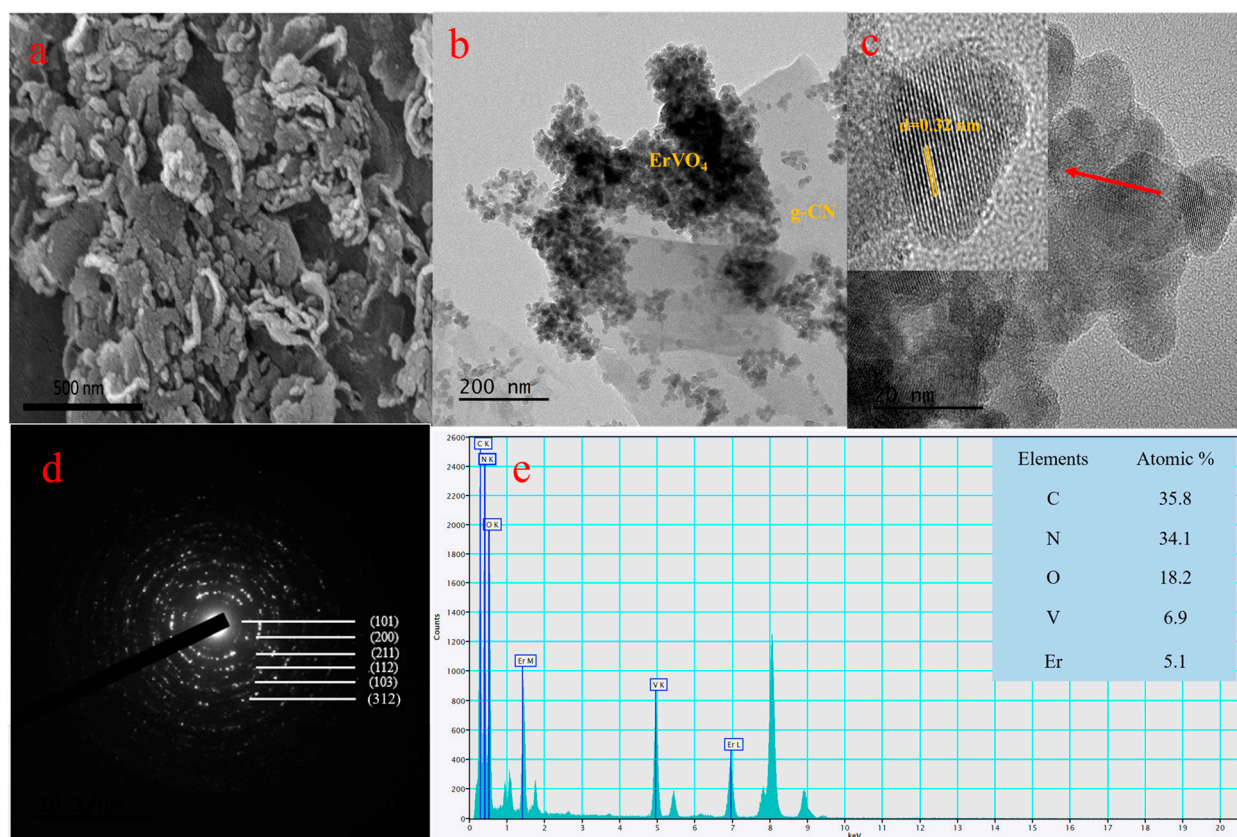


Figure 2. (a) FE-SEM images of ErVO_4 @g-CN. (b) HR-TEM images of ErVO_4 @g-CN. (c) Lattice fringe pattern of ErVO_4 and corresponding (d) SAED pattern of composite ErVO_4 @g-CN. (e) Atomic percentages from EDS analysis of C, N, O, V, and Er elements.

3.2. Electrochemical Analysis in $[\text{Fe}(\text{CN})_6]^{3-/4-}$ Solution

EIS can determine electrical responses between electrolytes, the interface of modified electrodes, and redox reactions, which helps us to further understand the system's mass transfer, charge transfer, and diffusion processes. The Nyquist plot is designed with a real part (Z') and an imaginary part (Z''). The Nyquist plot provides frequency-dependent resistance data equivalent to Randles' circuit. R_s , C_{dl} , R_{ct} , and Z_w are the resistance of solution (supporting electrolyte), double layer capacitance at the electrode surface,

charge transfer resistance, and the Warburg impedance in the circuit, as seen in Figure 3a. The prepared modified electrode was immersed in a solution of 0.1 M KCl containing 5.0 mmol/L of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ with reference and counter electrodes. Resistance changes of bare GCE, ErVO_4/GCE , $\text{g-CN}/\text{GCE}$, and $\text{ErVO}_4@\text{g-CN}/\text{GCE}$ are shown in Figure 3a, and the consecutive R_{ct} values are 321.59 Ω , 50.31 Ω , 58.90 Ω , and 32.42 Ω . As can be seen, the composite-coated modified electrode has the smallest semicircle due to the increase in electron transfer at the electrode surface with nano $\text{ErVO}_4@\text{g-CN}$.

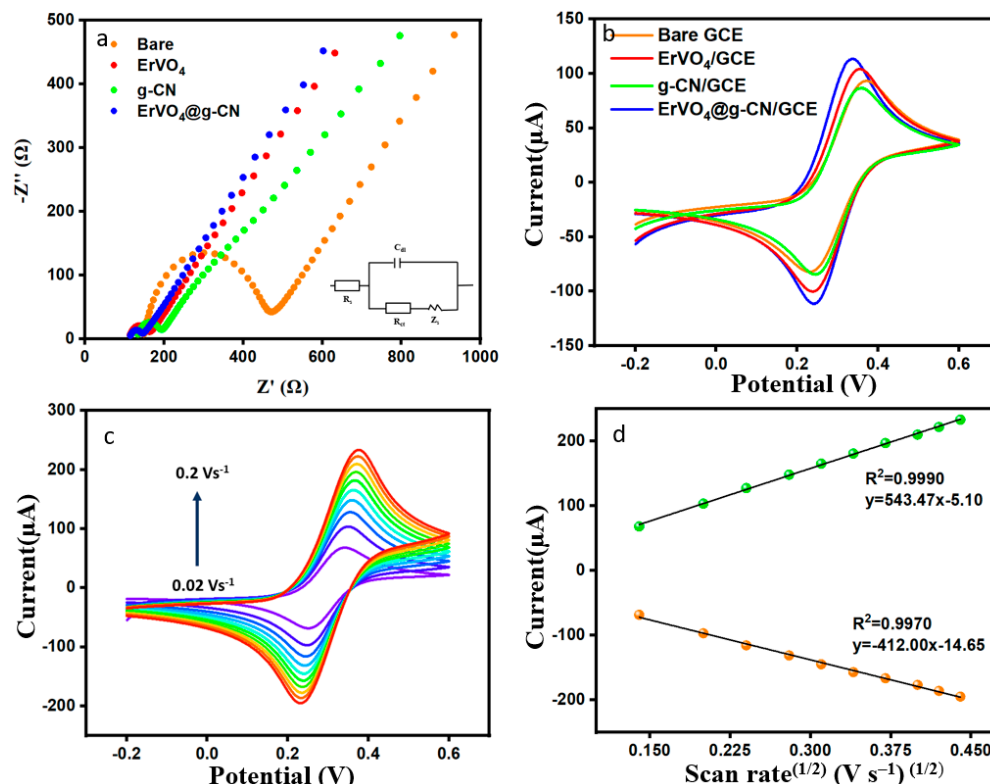


Figure 3. (a) EIS and (b) CV measurements of bare GCE, ErVO_4/GCE , $\text{g-CN}/\text{GCE}$, and $\text{ErVO}_4@\text{g-CN}/\text{GCE}$. (c) Different scan rates for $\text{ErVO}_4@\text{g-CN}/\text{GCE}$ in the presence of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and 0.1 M KCl and (d) Corresponding plot of current vs. square root of scan rate.

Performance of the electrochemical process was continued in order to optimize the modified electrode. Like the EIS, the experiment was carried out in 0.1 M KCl containing 5.0 mmol/L $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at a scan rate of 0.05 V s^{-1} in potential between -0.2 and 0.6 V. As can be seen in Figure 3b, the anodic peak currents of bare GCE, ErVO_4/GCE , $\text{g-CN}/\text{GCE}$, and $\text{ErVO}_4@\text{g-CN}/\text{GCE}$ were given consecutively at 92.87, 104.16, 85.65, and 114.34 μA , and the lowest potential difference of 0.09 V (peak separation, $\Delta E_p = E_{p,a} - E_{p,c}$) was obtained for $\text{ErVO}_4@\text{g-CN}/\text{GCE}$. Figure 3c shows the CV in different scan rates obtained from 0.02 to 0.2 V s^{-1} solution with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl. The peak currents increase with an increasing scan rate. Figure 3d displays a corresponding linear graph of I_p vs. $(\text{scan rate})^{1/2}$. The good linearity of the graph implies the diffusion control process of the electrochemical reaction. The Randles–Sevcik equation (Equation (1)) is used to calculate the electrochemically active surface area (EASA) of the electrode [38].

$$I_p = 2.69 \times 10n^{3/2}AD^{1/2}Cv^{1/2} \quad (1)$$

where,

I_p = Redox peak current

n = Number of electrons participating in the reaction ($n = 1$)

A = EASA

D = Diffusion coefficient ($7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)

C = Concentration of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ (0.005 M)

v = Scan rate (0.05 V s^{-1})

A better reversible reaction can be obtained in the presence of the $\text{ErVO}_4/\text{g-CN}$ composite, and this modified electrode can contribute an electrochemically active surface area (EASA) of 0.2 cm^2 to the system.

3.3. Electrochemical Analysis

3.3.1. Electrochemical Behaviors toward DMZ Detection

Dimetridazole (DMZ) is a derivative of the nitroimidazole drug that treats bacterial infections in veterinary medicine. Thus, the need for a sensitive and effective sensor for the detection of drugs which cause allergies is essential. Carbon-based composite modified electrodes have received more attention in recent years due to their high sensitivity and selectivity. Before carrying out the experiment in the presence of DMZ, the current responses for bare GCE, ErVO_4/GCE , $\text{g-CN}/\text{GCE}$, and $\text{ErVO}_4/\text{g-CN}/\text{GCE}$ in 0.1 M PBS (pH = 7) were analyzed (Figure S1), followed by the electrochemical responses for all electrodes toward 200 μM of DMZ and of PBS (pH 7.0) by cyclic voltammetry with a scan rate of 0.05 V s^{-1} , as shown in Figure 4a,b. The reduction peak potential of modified $\text{ErVO}_4/\text{g-CN}/\text{GCE}$ had a highest recorded value (20.89 μA) at -0.68 V , producing a better-defined peak than the bare electrode. The efficiency of a material-coated electrode was further examined with different coating of $\text{ErVO}_4/\text{g-CN}/\text{GCE}$ (2, 4, 6, 8, and 10 μL), by dropcasting method as shown in Figure 4c,d; the 8 μL -coated electrode was modified for further electrochemical studies.

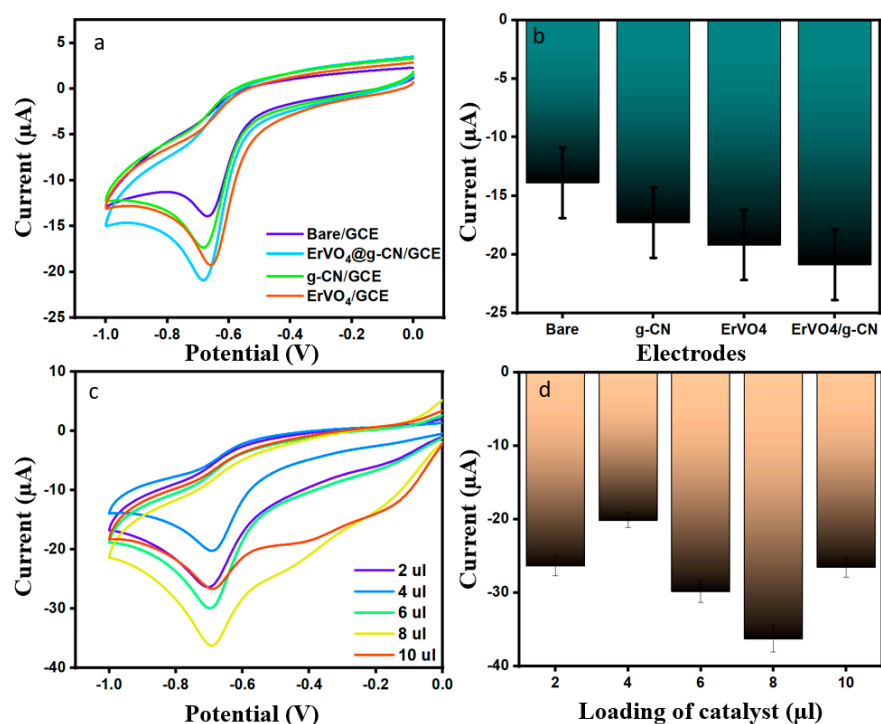


Figure 4. (a,b) CV profiles of bare GCE, ErVO_4/GCE , $\text{g-CN}/\text{GCE}$, and $\text{ErVO}_4/\text{g-CN}$ -modified GCEs in the presence of 200 μM DMZ at a scan rate of 50 mV s^{-1} in 0.1 M PBS (pH 7) and corresponding bar graph (c,d) Current changes in different catalyst amounts in the presence of 200 μM DMZ and 0.1 M PBS (pH 7) and corresponding bar graph.

3.3.2. Effect of pH

The influence of different pH values (3, 5, 7, 9, and 11) on current was investigated in the presence of 200 μM DMZ (scan rate 50 mV s^{-1}) for $\text{ErVO}_4/\text{g-CN}/\text{GCE}$. It can be seen in Figure 5a,b that I_p increases from pH 3 to 7 and decreases from pH 7 to 11. The data

show that E_{pc} was shifted toward a negative potential with an increasing pH (7–11) due to low current density hydrogen ions. It is shown that a maximum reduction current of $-20.91 \mu\text{A}$ was obtained when pH 7 was used in the medium, as indicated by the equal numbers of proton and electron transfers in the reaction; for this reason, pH 7 can be used for any further analyses [39].

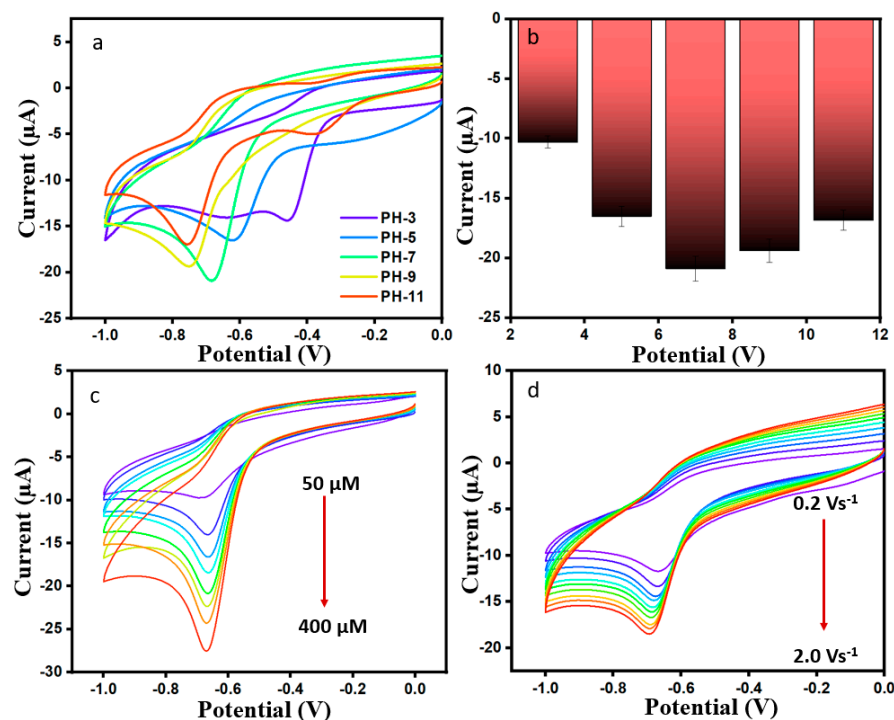


Figure 5. (a,b) CV curves of varying pH (3–11) for $\text{ErVO}_4\text{@g-CN/GCE}$. (c) Current responses for $\text{Er-VO}_4\text{@g-CN/GCE}$ at different concentrations of DMZ and corresponding linear plot. (d) CV curves of different scan rates in $200 \mu\text{M}$ DMZ and 0.1 M PBS and corresponding calibration plot for current vs. different (scan rate)^{1/2}.

3.3.3. Effect of Concentration and Scan Rate

By changing concentration, performance can be optimized for further electrochemical performance. Figure 5c shows the cyclic voltammogram for a modified $\text{ErVO}_4\text{@g-CN/GCE}$ electrode current response with changes in the concentration of 50 to $400 \mu\text{M}$ of DMZ in 0.1 M PBS with pH 7 at a scan rate of 50 mV s^{-1} . Current values increased linearly with increasing DMZ concentration as shown in Figure S3a. The linear relation of current vs. concentration is $I = -0.04649C - 8.72$ ($R^2 = 0.9831$). Also, a reduction peak current was studied for different scan rates from 20 to 200 mV s^{-1} , as shown in Figure 5d. Negative current peaks were linearly increased when analyzing the increasing scan rates, indicating a faster charge transfer. A linear regression equation of $I = -0.6807C - 8.833$ with $R^2 = 0.9941$ in current vs square root of scan rate graph in Figure S3b, conveys that DMZ is under a diffusion-controlled process.

3.3.4. Differential Pulse Voltammetry (DPV) Study for Determination of DMZ and Real Sample Analysis

The DPV method has a higher accuracy of sensitivity for electrochemically active substances. This experiment used a 0.1 M PBS in potential between -0.1 V and 0 V , a pulse amplitude of 0.05 V , a pulse time of 0.5 s , and a scan rate of 50 mV s^{-1} throughout the addition of DMZ from $0.5 \mu\text{M}$ to $863.5 \mu\text{M}$. Figure 6a,b show the DPV performance and corresponding calibration plot. I_{pa} increases linearly, and the linear regression equation is $y = -0.0195x - 4.5369$ ($R^2 = 0.9931$). The limit of detection and sensitivity are calculated

from using Equations (2) and (3) below [40]. Here, calculated values of the LOD and sensitivity are $0.001 \mu\text{M}$ and $2.523 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^2$, respectively.

$$\text{Limit of detection} = \frac{3 \times \text{Standard deviation}}{\text{Slope}} \quad (2)$$

$$\text{Sensitivity} = \frac{\text{Slop value of low concentration}}{\text{Electrode surface area}} \quad (3)$$

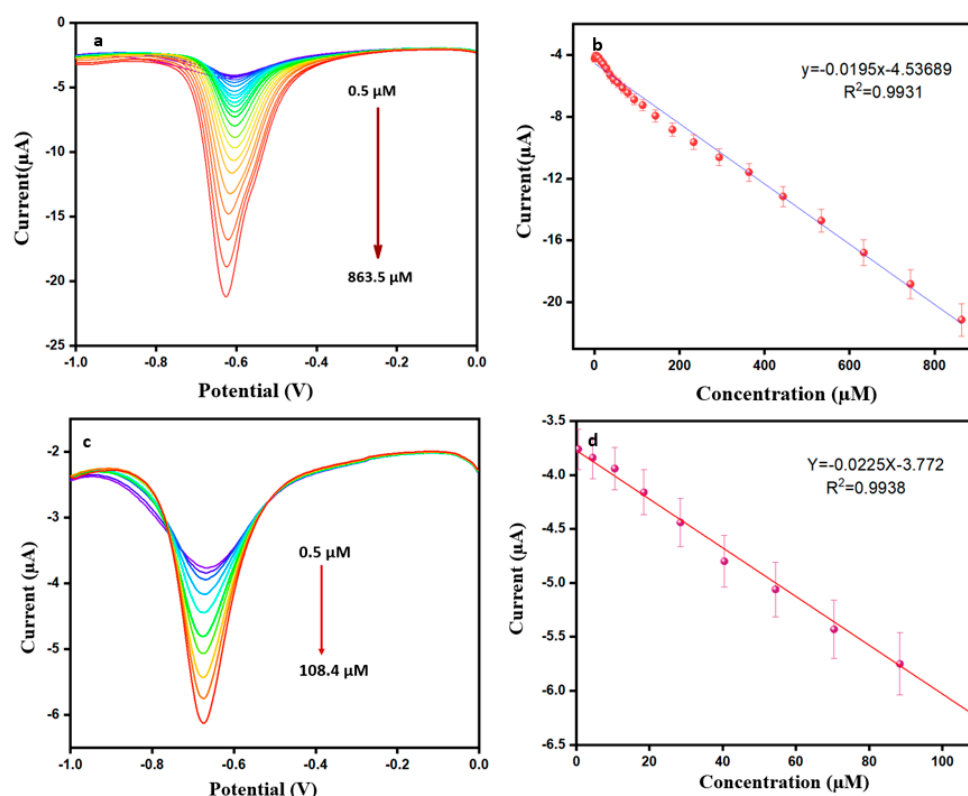


Figure 6. (a) DPV response for modified ErVO₄@g-CN/GCE toward DMZ (in pH = 7 PBS). (b) Corresponding calibration plot of current vs. concentration. (c) DPV response for milk sample toward ErVO₄@g-CN/GCE. (d) Corresponding calibration plot of current vs. concentration for milk sample.

The modified electrode of ErVO₄@g-CN/GCE was applied in real samples for the determination of DMZ. Milk was collected from a shopping mart for the DPV analysis. Then, 10 μL of milk was injected into 10 mL of PBS and centrifuged; a known amount of 0.001 M of DMZ was then added. For further experiments, an analysis of the solution was carried out using previously optimized conditions. The resultant current response and calibration plot are shown in Figure 6c,d. The response obtained from the DPV shows that this system can detect DMZ in these real samples, providing good results at potential at -0.683 V ; the LOD value was $0.008 \mu\text{M}$ for the real sample.

3.3.5. Selectivity, Reproducibility, Repeatability and Stability

We studied the interference of co-existing substances in the DMZ sample and inspected for selectivity of the modified electrode. Current response to the addition of interference compounds is presented in Figure 7a as well as in the relative bar diagram of Figure 7b. The studies for the ErVO₄@g-CN/GCE electrode was performed by adding $20 \mu\text{M}$ of ascorbic acid, uric acid, glucose, K^+ , Zn^{+2} , and Ca^{+2} each in the presence of 0.01 M DMZ. It was observed that the ErVO₄@g-CN/GCE-modified electrode showed good current response toward DMZ and had no significant interferences from co-interfering compounds.

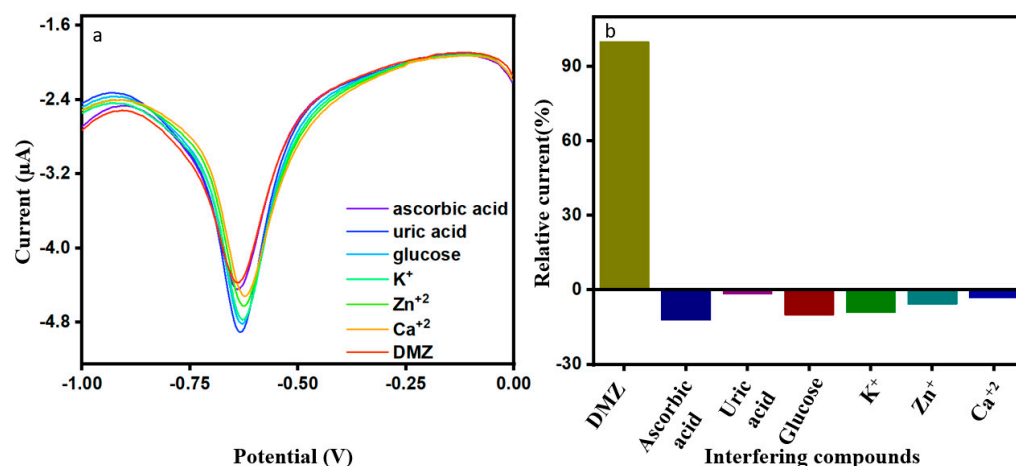


Figure 7. (a,b) DPV response of 20 μM of DMZ in the presence of co-interfering compounds; and the corresponding bar graph.

The experiment of repeatability and the respective bar diagram for the modified electrode in DMZ was used six times, as can be seen in Figure 8a,b, and in the same condition as before; the RSD value for the six trials is 2.01%. The reproducibility of ErVO₄@g-CN/GCE was investigated for three different electrodes in 0.01 M of 100 μL DMZ, as shown in Figure 8c; the corresponding bar diagram is shown in Figure S4. The above-mentioned test gave a relative standard deviation (RSD) of 2.97% and, thereby, along with the obtained RSD values of reproducibility and repeatability, indicates a good performance for the DMZ sensor. Furthermore, the stability of DMZ was evaluated for 60 cycles in the presence of 0.01 M of DMZ and pH 7 phosphate buffer solution; Figure 8d displays the result. The current response of modified ErVO₄@g-CN/GCE has good stability in the DMZ environment [41,42].

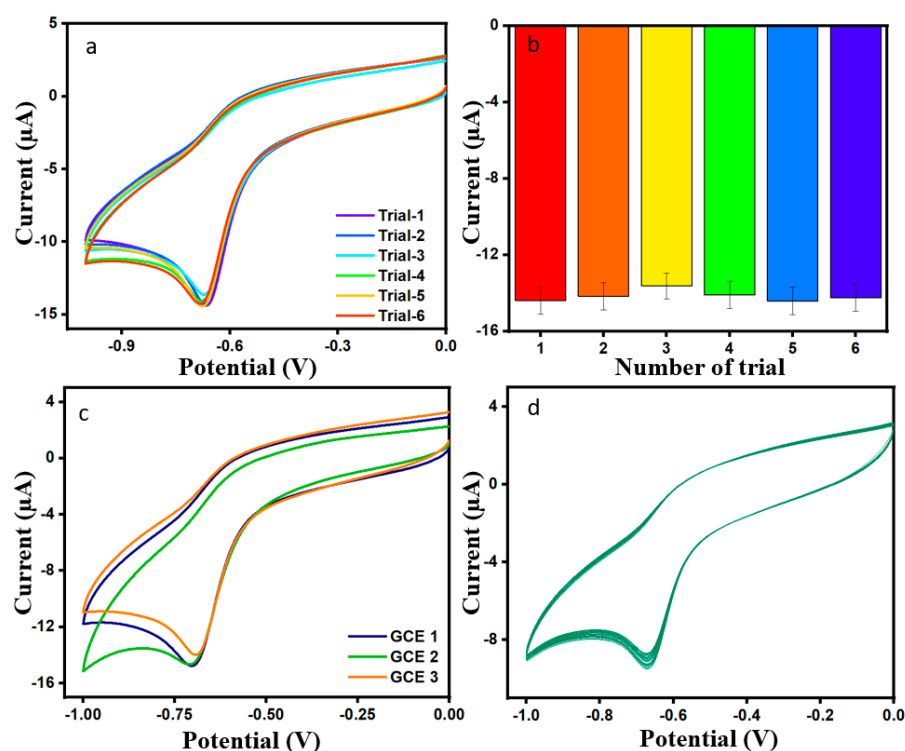


Figure 8. (a,b) Plot of repeatability in the presence of DMZ 100 μM and correlated bar graph. (c) CV plot of reproducibility in the presence of DMZ 100 μL and pH = 7 PBS. (d) CV plot of cycle stability for 60 cycles in the presence of DMZ (100 μM) and pH = 7 PBS.

4. Conclusions

In this research study, we successfully developed nano-sized ErVO_4 via the hydrothermal method for a modified $\text{ErVO}_4/\text{g-CN}/\text{GCE}$ -based electrochemical sensor for detecting DMZ. The composite was examined with XRD, EDS, and HR-TEM, and the confirmed crystal structure was discussed. The rare earth metal vanadate with a two-dimensional structure modified electrode contributed modified electrodes that revealed excellent electrocatalytic activity with respect to individual and bare electrodes. Furthermore, $\text{ErVO}_4/\text{g-CN}/\text{GCE}$ resulted in a lower limit of detection of $0.001 \mu\text{M}$ toward DMZ in the wide working range of 0.5 to $863.5 \mu\text{M}$ by the differential pulse voltammetry method. This $\text{ErVO}_4/\text{g-CN}$ -coated modified electrode system reported a highly active surface area, high conductivity, and less charge transfer resistance. Furthermore, the proposed $\text{ErVO}_4/\text{g-CN}/\text{GCE}$ sensor showed good selectivity toward DMZ compared with six different interfering compounds (ascorbic acid, uric acid, glucose, K^+ , Zn^{+2} , and Ca^{+2}) from DPV electrochemical analysis, and good cycle stability was also observed for 60 cycles. Finally, it was found that the above-discussed electrochemical sensor shows promise in being able to recognize DMZ in actual samples.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/s24061808/s1>, Chemicals and reagents; Figure S1. CV measurements of bare GCE, ErVO_4/GCE , $\text{g-CN}/\text{GCE}$, and $\text{ErVO}_4/\text{g-CN}/\text{GCE}$ of composite in PBS (pH = 7); Figure S2. (a) HR-TEM image of $\text{ErVO}_4/\text{g-CN}$ composite. (b–f) Elemental mapping of Er, V, O, C, and N; Figure S3. (a) Corresponding linear plot (for Figure 5c) of current vs concentration. (b) corresponding calibration plot for (Figure 5d) of current vs. different (scan rate) $^{1/2}$; Figure S4. Corresponding bar graph for reproducibility in the presence of DMZ $100 \mu\text{L}$ and pH = 7 PBS.

Author Contributions: U.G.A.S.: Conceptualization, Writing—original draft, Writing—review & editing, Methodology, Data curation, Visualization, Formal Analysis; S.-F.W.: Supervision, Funding acquisition, Investigation, Validation, Resources. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: Data is contained within the article or Supplementary Materials.

Acknowledgments: This work was financially supported by the National Taipei University of Technology (NTUT).

Conflicts of Interest: The authors declare no conflicts of interest.

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