

Article

N,S-Donor Triazole–Thione-Modified Graphite Paste Electrode for Selective Voltammetric Detection of Cu(II) in Environmental Waters

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Abstract

A simple and cost-effective graphite paste electrode modified with 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione was developed for the selective voltammetric determination of Cu(II) ions in environmental water samples. The N,S-donor ligand was incorporated into a graphite–polystyrene matrix without the use of nanomaterials, providing a reproducible and straightforward electrode fabrication route. Scanning electron microscopy revealed a rough, porous surface morphology with an enhanced electroactive surface area of 0.065 cm², approximately twice the geometric area. Electrochemical impedance spectroscopy confirmed diffusion-controlled mass transport, while cyclic voltammetry indicated quasi-reversible behaviour of the Cu(II)/Cu(0) redox system with a linear dependence of peak current on the square root of the scan rate. Differential pulse voltammetry under optimised conditions (0.1 mol·L^{−1} H₂SO₄, pH 1.0–1.2) yielded a linear analytical response over the concentration range of 0.01–0.4 μmol·L^{−1} (R² = 0.99507), with a limit of detection of 0.02 μmol·L^{−1} and a limit of quantification of 0.06 μmol·L^{−1}—well below the WHO guideline for copper in drinking water. The sensing mechanism involves selective N,S-bidentate coordination of Cu(II) at the electrode surface, followed by electrochemical reduction, as supported by FT-IR spectroscopic evidence. The sensor demonstrated good selectivity toward Cu(II) in the presence of common interfering metal ions at up to 20-fold excess. The method was successfully validated against ICP-OES (recovery 99.8%, RSD < 0.33%) and confirmed by spike–recovery experiments (99.0–99.5%), confirming its practical applicability for trace-level environmental monitoring. The modified electrode retained approximately 93% of its initial response after 30 consecutive measurements and 91% after 14 days of storage, demonstrating good operational stability.

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Keywords: copper(II) determination; graphite paste electrode; triazole–thione ligand; N,S-donor coordination; differential pulse voltammetry; environmental water analysis

1. Introduction

Copper is one of the most widely used transition metals due to its high electrical and thermal conductivity, mechanical flexibility, and extensive application in electrical engineering, metallurgy, catalysis, and environmental technologies. The intensive exploitation of copper-containing materials and the generation of industrial and technogenic wastes have resulted in the release of Cu(II) ions into natural water systems, soils, and industrial effluents. At elevated concentrations, Cu(II) ions pose a potential environmental risk and may cause toxic effects in living organisms, whereas at trace levels copper remains an essential biogenic element [1]. Therefore, the development of reliable, sensitive, and selective analytical methods for the determination of Cu(II) ions in environmental and technogenic matrices is of significant importance. Conventional techniques for copper determination, laser-induced breakdown spectroscopy and laser ablation inductively coupled plasma mass spectrometry [2], Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) [3,4], and fluorescence-based methods [5,6] provide excellent sensitivity and accuracy; however, they require expensive instrumentation, complex sample preparation, and laboratory-based operation. Spectroscopic methods such as Fourier-transform infrared spectroscopy (FT-IR) [7] are primarily applied for structural characterization and complexation studies rather than for direct quantitative determination of metal ions. In contrast, electrochemical methods offer several advantages, including simplicity, low cost, portability, rapid response, and high sensitivity, making them particularly attractive for on-site and routine analysis of heavy metal ions. In recent years, considerable attention has been devoted to the development of electrochemical sensors for Cu(II) detection through electrode surface modification. Today, modern electrochemical methods are regarded as promising approaches for the determination of ions such as Hg(II), Cd(II), Pb(II), Cu(II), and others [8].

Numerous electrochemical platforms have been developed for the determination of Cu(II) ions, including graphene-based nanocomposites, conducting polymers, mercury electrodes, and optical sensing systems. While many of these approaches provide excellent analytical performance, their practical application is often limited by the use of expensive nanomaterials, multistep fabrication procedures, environmentally hazardous mercury components, or sophisticated instrumentation. Consequently, there remains a continuing need for simple, reproducible, cost-effective, and environmentally sustainable sensing platforms suitable for routine monitoring of trace copper contamination in natural waters.

Among the various coordination-based sensing materials, N,S-donor heterocyclic ligands have attracted considerable attention because of their strong affinity toward Cu(II) ions, high complex stability, and enhanced selectivity arising from synergistic nitrogen–sulfur coordination. Triazole–thione derivatives are particularly promising in this regard, as they possess multiple donor sites capable of forming stable coordination complexes with transition metal ions. Nevertheless, despite their well-established role in coordination chemistry, the use of triazole–thione compounds as modifiers of graphite paste electrodes for Cu(II) sensing has received only limited attention.

To the best of our knowledge, the application of 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione as a functional modifier for graphite paste electrode-based Cu(II) detection has not been previously reported. The proposed sensing platform combines straightforward electrode fabrication with coordination-driven preconcentration of Cu(II)

ions through N,S-donor binding sites, while avoiding the use of nanomaterials, toxic mercury electrodes, and organic solvent systems. Such features make the developed sensor attractive for practical environmental applications.

The aim of this work was to develop and validate a triazole–thione-modified graphite paste electrode for the selective voltammetric determination of trace Cu(II) ions in environmental water samples. Particular attention was devoted to elucidating the electrochemical and coordination mechanisms responsible for signal generation and to evaluating the practical applicability of the proposed method through the analysis of real reservoir water samples with validation against ICP-OES measurements.

2. Materials and Methods

2.1. Instruments and Reagents

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) analyses were carried out using a Corrtest CS100 potentiostat/galvanostat (Wuhan Corrtest Instruments Corp., Ltd., Wuhan, China) connected to an HP ProBook 450 15.6-inch G10 laptop computer (HP Inc., Palo Alto, CA, USA). A graphite paste electrode modified 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione was used as the working electrode. The electrode length was 60 mm, and its geometric surface area was calculated to be 0.0314 cm².

A silver/silver chloride (Ag/AgCl, 1 mol·L⁻¹ KCl) (ΔITTA.01.0100 CB; NPP Tomanalyt, Tomsk, Russia) electrode was used as the reference electrode, while a glassy carbon electrode (15221160712, Shanghai Sanjue Industrial Co., Ltd., Shanghai, China) served as the counter electrode. The experiments were performed in a 30 mL quartz electrochemical cell.

A BIOBASE MS7-H550S magnetic stirrer (BIOBASE Group, Jinan, Shandong, China) was used to ensure uniform distribution of ions at the electrode surface. All solutions were prepared using bidistilled water (Heal Force Bio-Meditech Holdings Ltd., Shanghai, China). Measurements were carried out using a BIOBASE BA504B analytical balance (BIOBASE Group, Jinan, Shandong, China). The surface morphology was investigated by scanning electron microscopy (SEM) using a JEOL JSM-IT200LA (JEOL Ltd., Akishima, Tokyo, Japan) instrument.

The organic modifier 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione was synthesized at the S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Uzbekistan Academy of Sciences. Copper(II) sulfate pentahydrate (CuSO₄·5H₂O, GOST 19347-99), sulfuric acid (H₂SO₄, GOST 4204-77), polystyrene, graphite powder (Sigma-Aldrich, St. Louis, MO, USA; CAS No. 7782-42-5), acetone (snabtechmet.uz, GOST 2603-79), copper wire (GOST 22666-2016, Uzbekistan), ammonium hydroxide, concentrated nitric acid (HNO₃) and potassium chloride (99.0%) were used in this study. All other chemicals and reagents employed were of analytical grade and were used without further purification. All aqueous solutions were prepared using deionized water with a resistivity of ≥18.2 MΩ·cm (Milli-Q quality), obtained from a HEAL FORCE CR-Easy15 water purification system (Heal Force Bio-Meditech Holdings Ltd., Shanghai, China).

2.2. Preparation of the Electrolyte Solution for Electrochemical Analysis

2.2.1. Preparation of a 0.1 M Standard Cu(II) Ion Solution

A 0.10 mol·L⁻¹ solution was prepared by dissolving 25.0 g of CuSO₄·5H₂O in a 1000.0 mL volumetric flask and diluting to the mark with bidistilled water. From the 0.10 mol·L⁻¹ stock solution, working solutions in the concentration range from 0.010 mol·L⁻¹ to 0.00010 mol·L⁻¹ were prepared.

2.2.2. Preparation of the Supporting (Background) Electrolyte Solution

A 100.0 mL portion of 1.0 mol·L⁻¹ H₂SO₄ solution was prepared from a certified standard solution. This stock solution was then diluted to obtain a series of solutions with pH values of approximately 3.5, 3.0, 2.5, 2.0, and 1.0–1.2.

2.3. 5-(4-Aminophenyl)-4-Amino-1,2,4-Triazole-3(2H)-Thione

A literature survey indicates that organic ligands containing thione and thiol functional groups form highly stable complexes with Cu(II) ions [9]. These ligands coordinate through nitrogen and sulfur donor centers, enabling strong interactions with metal ions and thereby enhancing selectivity. Consequently, thione–thiol ligands bearing N,S-donor atoms are regarded as promising modifiers for the development of highly sensitive and selective electrochemical sensors for Cu(II) determination.

5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione (Figure 1) was synthesized by refluxing 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thione in 80% hydrazine hydrate for 8 h. As a result of the reaction, the compound was obtained as white crystals with a yield of 72%. The structure of the obtained compound was confirmed by FT-IR and ¹H NMR spectroscopy, as well as by thin-layer chromatography (TLC) analysis. The reaction mechanism can be explained by the nucleophilic addition of hydrazine to the thiocarbonyl group, followed by the opening of the oxadiazole ring and subsequent heterocyclization leading to the formation of the 1,2,4-triazole ring. Detailed information about the synthesis procedure is provided in Appendix A.

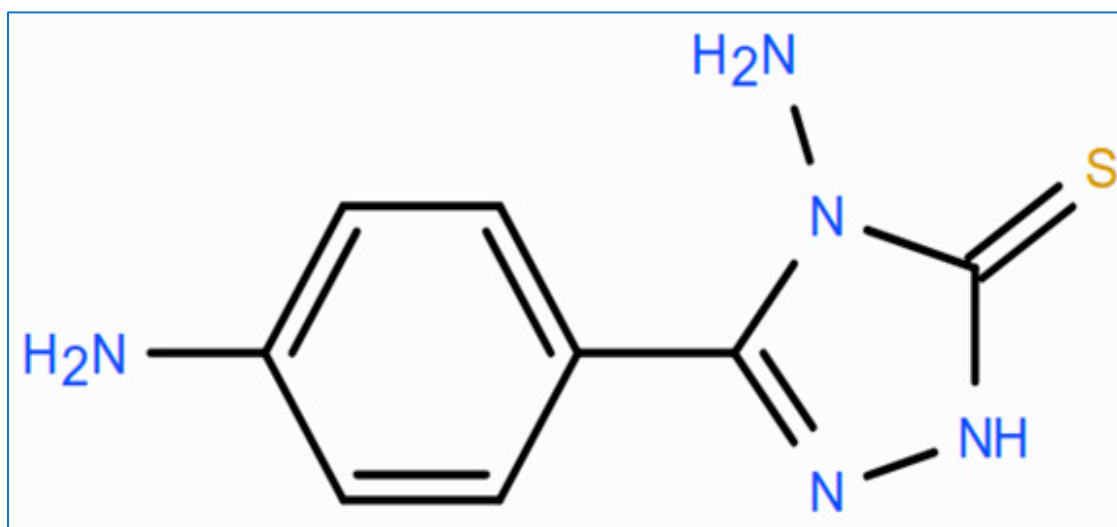


Figure 1. Chemical structure of 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione.

2.4. Binding Mechanism of Cu(II) Ions at the Surface of the Electrode Modified with 5-(4-Aminophenyl)-4-Amino-1,2,4-Triazole-3(2H)-Thione

Since the organic modifier 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione is not soluble in aqueous media, its electrochemical behavior could not be directly investigated in the dissolved (solution) state. Instead, the modified graphite electrode (MGE) itself was examined by cyclic voltammetry and differential pulse voltammetry in the aqueous supporting electrolyte solution in the absence of Cu(II) ions. Under these conditions, no distinct redox peak or analytical signal attributable to the modifier alone was observed within the investigated potential window, confirming that the electrochemical response reported in this work originates specifically from the Cu(II)/Cu(0) redox process at the modified electrode surface rather than from any intrinsic redox activity of the modifier itself.

FT-IR spectra were studied to evaluate the interaction between Cu(II) ions and the modifier 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione (Figure 2). After interaction with Cu(II) ions, slight shifts were observed in the absorption bands corresponding to -NH/NH_2 , C=N , C-N , and thione/thiol groups. In particular, the changes in the $1600\text{--}1400\text{ cm}^{-1}$ region indicate the participation of nitrogen atoms of the triazole ring in coordination. In addition, the changes observed in the $1260\text{--}1180\text{ cm}^{-1}$ and $600\text{--}400\text{ cm}^{-1}$ regions can be attributed to the involvement of sulfur-containing groups and the formation of Cu–N/Cu–S coordination bonds. These results confirm that Cu(II) ions are mainly bound to the modifier surface through N and S donor centers. Many heterocyclic thione derivatives bearing -N and -S donor centers exhibit tautomeric equilibrium in solution between the thione (C=S) and thiol (-SH) forms. The electronic structure of heterocyclic thione derivatives and the existence of the thiol–thione tautomeric equilibrium have been reported in the literature [10].

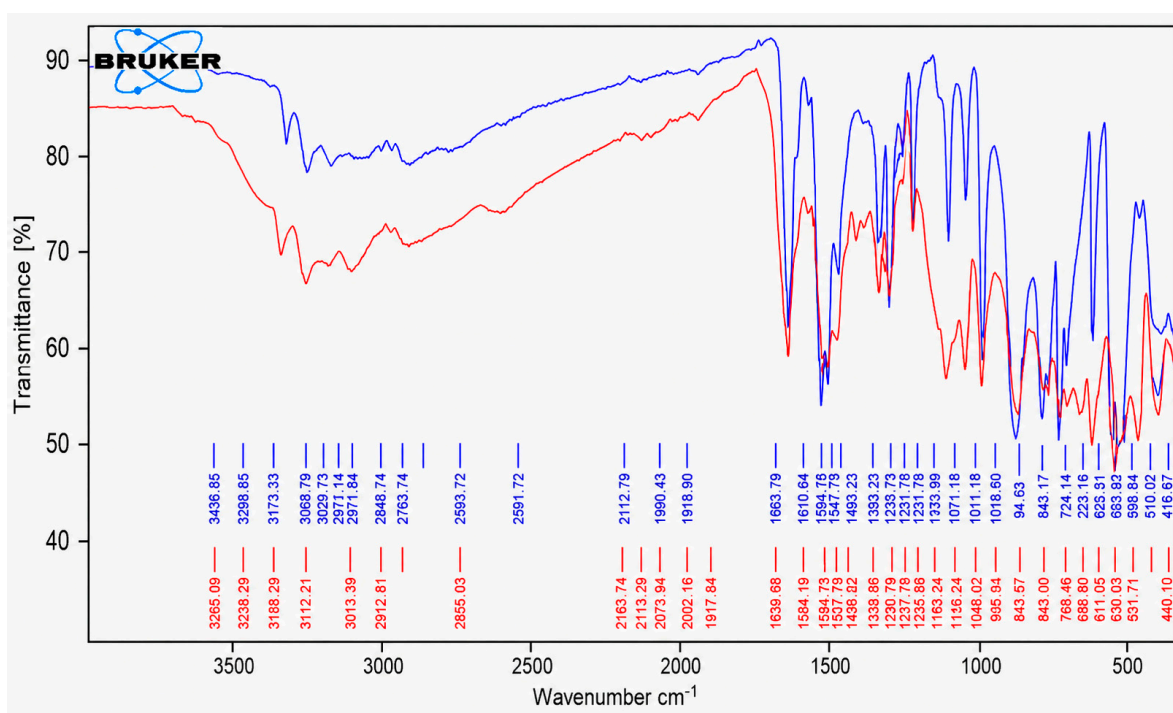


Figure 2. FT-IR spectra of 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione before and after complexation with Cu(II): blue line—free ligand; red line—Cu(II) complex.

During the complex formation process, the thiol group undergoes deprotonation to yield the thiolate species (-S^-) [11], which subsequently coordinates to the Cu(II) ion, while the triazole ring binds through its nitrogen atom. As a result, an N,S-type bidentate ligand is formed. Cu(II) ions generally adopt a square-planar or square-pyramidal coordination environment. In the resulting complex, the Cu(II) center is coordinated by two nitrogen atoms derived from two triazole rings and two sulfur atoms derived from two thiolate groups, generating a bidentate-type architecture. The proposed coordination structure of the complex is illustrated in Figure 3.

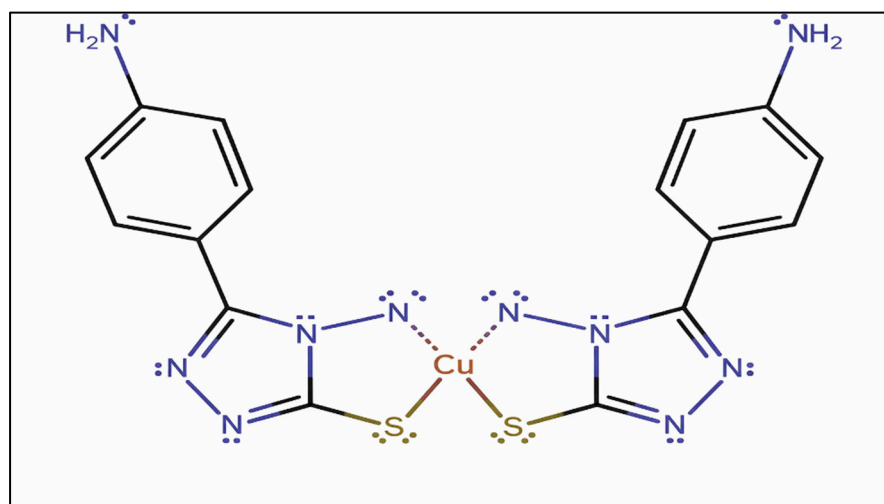
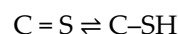
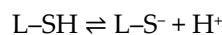


Figure 3. Proposed coordination structure of the Cu^{2+} complex with 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione.

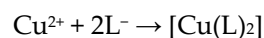
The complexation mechanism of Cu(II) ions with 5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione proceeds through several consecutive stages. These stages include tautomerization, deprotonation, and coordination with the metal ion. Initially, the ligand exhibits thione–thiol tautomerism in solution. During this process, the thione form ($\text{C}=\text{S}$) is converted into the thiol form ($\text{C}-\text{SH}$), thereby creating favorable conditions for subsequent coordination interactions:



In the formed thiol form, the dissociation of the hydrogen atom leads to deprotonation of the ligand, resulting in the formation of a thiolate anion that acts as a strong donor center:

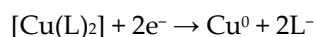


In the next stage, the deprotonated ligand interacts with the Cu(II) ion. Coordination occurs mainly through the sulfur atom of the ligand and the nitrogen atom of the triazole ring. As a result, the ligand behaves as an N,S-bidentate ligand and forms a stable complex with Cu(II) :

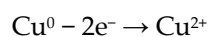


In the resulting complex, an N_2S_2 coordination environment is formed around the Cu(II) ion through the participation of nitrogen and sulfur donor atoms. Such a structure enhances the stability of the complex and significantly affects the electron density and overall electrochemical properties of the Cu(II) ion.

On the electrode surface, this Cu(II) complex subsequently undergoes an electrochemical reduction process. During reduction, the Cu(II) ion in the complex is converted into metallic Cu(0) , while the ligand returns to its free or coordinatively active form:



During the subsequent anodic sweep, the deposited Cu(0) is oxidized back to Cu(II) , returning to the solution:



This anodic oxidation step represents the reverse half of the same quasi-reversible Cu(II)/Cu(0) redox couple described above, and it is this anodic peak current that was used as the analytical signal for quantitative Cu(II) determination throughout this work.

Thus, the complex formation of Cu(II) ions with 5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione occurs through thione–thiol tautomerism of the ligand, followed by deprotonation and coordination of the resulting thiolate form with the metal ion.

It should be noted that the proposed N,S-coordination mechanism is supported by FT-IR spectroscopic evidence. The disappearance of the C=S stretching band at $\sim 1050\text{ cm}^{-1}$ and the shift in the C–S band upon complexation confirm the involvement of the sulfur donor center in coordination, consistent with previously reported thione–thiolate systems (Figure 2). The N–H stretching bands observed at 3268 cm^{-1} and 3351 cm^{-1} in the free ligand spectrum undergo a marked shift upon complex formation, further supporting coordination through the triazole nitrogen atom. These spectroscopic observations are consistent with the proposed N₂S₂ coordination mode and confirm that the binding mechanism operates through the N,S-donor centers of the ligand, rather than being inferred solely from structural analogies.

2.5. Preparation of the Modified Graphite Electrode

Today, in order to enhance the accuracy and sensitivity of electrochemical analysis of heavy metal ions, the modification of electrodes has become widely applied in practice. Various inorganic nanomaterials (metals and metal oxides, graphene, carbon nanotubes, etc.), organic substances (polymers and small organic molecules), and biomaterials [12] have been employed as modifiers, while composite graphite paste [13] and glassy carbon electrodes (GCEs) [14] are commonly used as binder bases for the electrode.

The electrode was fabricated in polystyrene tubes with a diameter of 2.0 mm, a geometric surface area of 0.0314 cm^2 , and a length of 60.0 mm. Electrodes prepared with different mass ratios were tested, and the optimal composition providing maximum electrical conductivity and sensitivity was determined to be 0.50:1.50:0.10 g (polystyrene: graphite: 5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione). Polystyrene was used as a matrix material to ensure mechanical stability [15].

To prepare the mixture, 0.50 g of polystyrene was dissolved in acetone, followed by the addition of 1.50 g of spectrally pure graphite and 0.10 g of the organic reagent 5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione. The resulting suspension was mechanically stirred for 10–20 min. The obtained paste was placed into a specially prepared tube containing a copper wire pretreated with concentrated nitric acid.

The unmodified graphite electrode was prepared in the same manner but without adding the organic reagent. The prepared electrodes were washed with ethanol and distilled water, dried, and then used for analysis. Acetone, used solely as the solvent for polystyrene, was removed by natural evaporation at room temperature; the freshly prepared electrodes were left to stand for approximately one week to ensure complete hardening of the electrode body and complete evaporation of residual acetone before use. This drying period was applied identically to all prepared electrodes in order to ensure the reproducibility of the electrode fabrication procedure. The effectiveness of this standardized drying protocol is further supported by the electrode-to-electrode reproducibility results presented in Section 3.6, where repeated measurements showed a relative standard deviation of 4.2% over 30 consecutive measurements and retention of 91% of the initial response after 14 days of storage.

The working electrode could be used for approximately 30–40 analytical measurements. After every 10–15 analyses, polishing and washing of the electrode surface were recommended.

2.6. Cyclic Voltammetric Analysis

Voltammetric measurements were performed in a conventional electrochemical cell with a total volume of 30.0 mL. A 0.1 mmol·L⁻¹ working Cu(II) solution, prepared by dilution of the 0.1 mol·L⁻¹ stock solution, was used for cyclic voltammetric measurements. The electrolyte solution consisted of 0.1 mL of the 0.1 mmol·L⁻¹ Cu(II) working solution, 2.0 mL of 0.1 mol·L⁻¹ H₂SO₄, and bidistilled water to a total volume of 25 mL.

A graphite electrode modified with 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione was used as the working electrode. An Ag/AgCl electrode served as the reference electrode, while a glassy carbon electrode (GCE) was employed as the counter electrode.

Cyclic voltammetry measurements were carried out at scan rates ranging from 0.03 to 0.1 V s⁻¹. After optimization of the experimental parameters, the potential window was fixed as follows: Estep1 = -0.5 V, Estep2 = 1.0 V, and Efinal = -0.5 V.

2.7. Differential Pulse Voltammetric Analysis

Voltammetric measurements were performed in a conventional electrochemical cell with a total volume of 30.0 mL. The electrolyte solution consisted of 0.010 μmol·L⁻¹; 0.040 μmol·L⁻¹; 0.080 μmol·L⁻¹; 0.120 μmol·L⁻¹; 0.160 μmol·L⁻¹; 0.180 μmol·L⁻¹; and 0.200 μmol·L⁻¹; 0.240 μmol·L⁻¹; 0.280 μmol·L⁻¹; 0.320 μmol·L⁻¹; 0.360 μmol·L⁻¹ 0.400 μmol·L⁻¹ standard Cu(II) solution, 2.0 mL of 0.1 mol·L⁻¹ sulfuric acid as the supporting electrolyte, and bidistilled water was added until the total volume of the solution reached 25 mL.

A graphite electrode modified with 5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione was used as the working electrode. An Ag/AgCl electrode served as the reference electrode, while a glassy carbon electrode (GCE) was employed as the counter electrode.

DPV parameters: pulse amplitude 50 mV, pulse width 50 ms, step potential 5 mV, accumulation potential +0.7 V, accumulation time 60 s, and scan range +0.7 to +0.1 V

3. Results and Discussion

3.1. Electrochemical and Morphological Characterization of the Modified Electrode

3.1.1. Voltammetric Characterization of the Modified Graphite Electrode

Preliminary studies were performed using cyclic voltammetry to evaluate the electrochemical behavior at the surface of the modified electrode. Cyclic voltammetry is an effective technique for investigating interfacial electrochemical processes and provides valuable information about the charge-transfer characteristics of the modified electrode. This approach contributes to a better understanding of the electrochemical properties of the system and improves the accuracy and reliability of electrochemical measurements.

To evaluate the electroactive properties of the prepared electrode surface and the efficiency of the electron transfer process, the 5 mmol·L⁻¹ [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ redox couple in 0.1 mol·L⁻¹ KCl supporting electrolyte was selected. The electrochemical cell was filled with 0.625 mL of 0.1 mol·L⁻¹ K₄[Fe(CN)₆], 0.625 mL of 0.1 mol·L⁻¹ K₃[Fe(CN)₆], and 23.75 mL of 0.1 mol·L⁻¹ KCl solution (total volume 25 mL). The potential window from -0.4 V to +0.7 V was chosen for recording the cyclic voltammogram.

The cyclic voltammetric parameters obtained at scan rates from 0.025 to 0.045 V·s⁻¹ are summarized in Table S1. As shown in Figure 4a,b, the modification of the graphite paste electrode with 5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione resulted in a markedly enhanced electrochemical response compared with the unmodified electrode. Specifically, the anodic peak current (I_{pa}) increased approximately 20-fold upon modification (e.g., from 7 × 10⁻⁴ A to 14.3 × 10⁻³ A at 0.025 V·s⁻¹), and the peak-to-peak separation (ΔE_p) decreased substantially from 0.375–0.46 V (unmodified) to 0.13–0.24 V (modified),

indicating significantly improved electron-transfer kinetics at the modified electrode surface. The half-wave potential ($E_{1/2}$) remained stable at approximately 0.17–0.19 V for both electrodes, confirming that the redox chemistry of the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ couple was not altered by the surface modification.

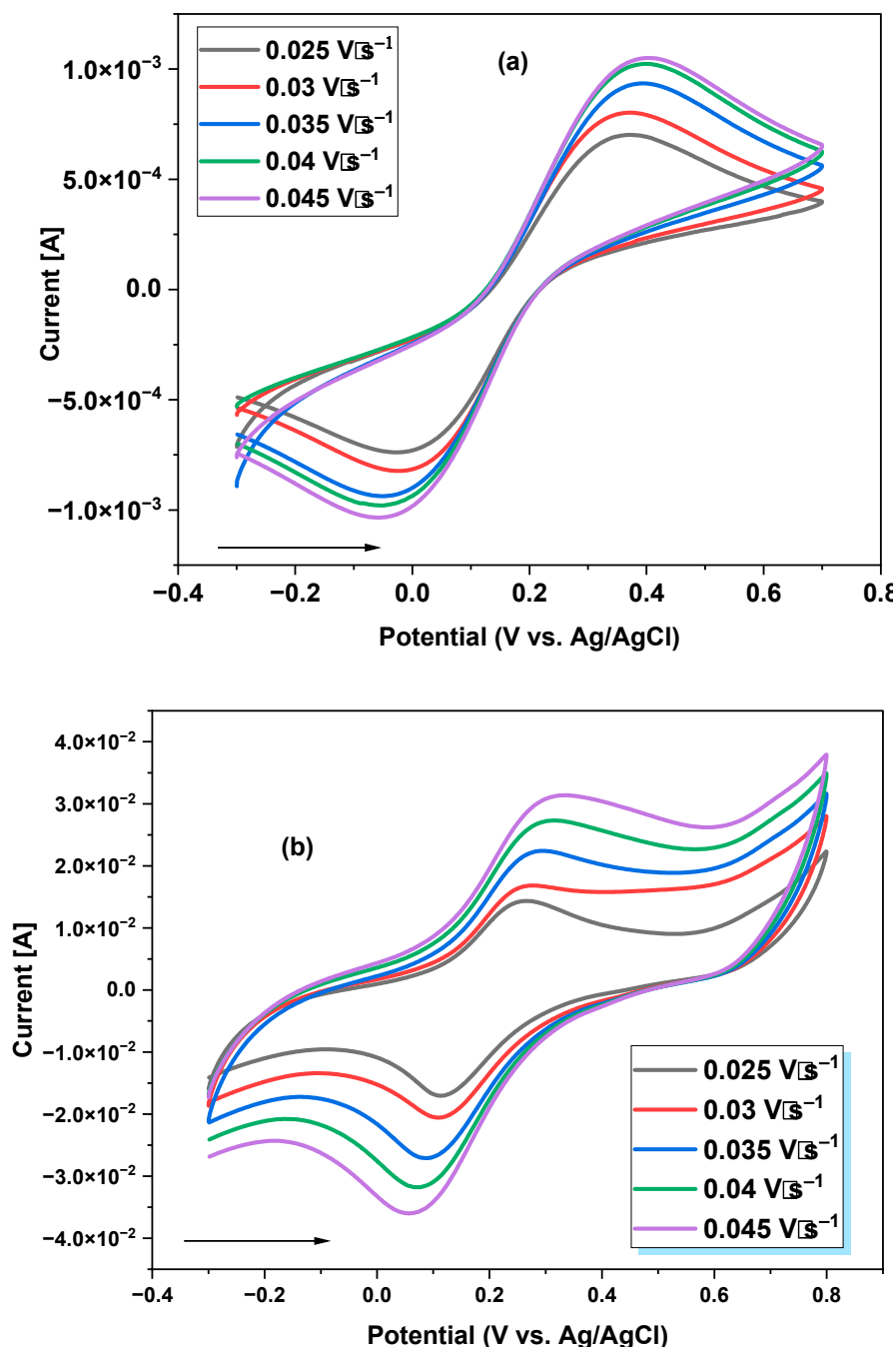


Figure 4. Cyclic voltammograms of 5 mmol·L^{−1} $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ in 0.1 mol·L^{−1} KCl at scan rates of 0.025–0.045 V·s^{−1} at (a) the unmodified and (b) the modified graphite paste electrode.

It should be noted that the relatively higher ΔE_p and lower peak currents observed for the unmodified electrode are consistent with the known insulating effect of the polystyrene binder used in the graphite paste matrix, which partially encapsulates graphite particles and reduces the density of accessible electroactive sites at the surface [16]. This behavior is characteristic of polymer-bound carbon composite electrodes and should not be interpreted as a sign of a poorly prepared electrode surface. Upon incorporation of the

N,S-donor triazole–thione ligand, the electroactive site density increases substantially, as confirmed by the calculated electroactive surface area of 0.065 cm^2 —approximately two-fold greater than the geometric area (0.0314 cm^2).

Based on the CV data presented in (Table S1), it can be observed that the modification of the graphite paste electrode with 5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione increases the electroactivity of the electrode surface and enhances the efficiency of the electron transfer process. According to Equation (1) and the Randles–Ševčík relationship, the electroactive surface area of the modified electrode was calculated to be 0.065 cm^2 .

$$I_p \propto \nu^{1/2} \quad (1)$$

where I_p is the peak current and $\nu^{1/2}$ is the square root of the potential scan rate.

Electrochemical Impedance Spectroscopy (EIS) Analysis of the Modified Graphite Paste Electrode.

Electrochemical impedance spectroscopy (EIS) was employed to investigate the electron-transfer characteristics at the electrode–solution interface of the modified graphite paste electrode and to determine the charge-transfer resistance (R_{ct}). This technique provides reliable information about interfacial electrokinetic processes and allows evaluation of the effectiveness of surface modification [17].

The impedance measurements were performed at a direct current (DC) potential of 0.175 V relative to the open-circuit potential (OCP) with an AC perturbation amplitude of 5 mV over a frequency range from 100 kHz to 0.01 Hz . The experiments were conducted in an electrolyte solution containing $5.0\text{ mmol}\cdot\text{L}^{-1}$ $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ as the redox probe and $0.10\text{ mol}\cdot\text{L}^{-1}$ KCl as the supporting electrolyte at $T = 298\text{ K}$. The corresponding Nyquist plots are presented in Figure 5.

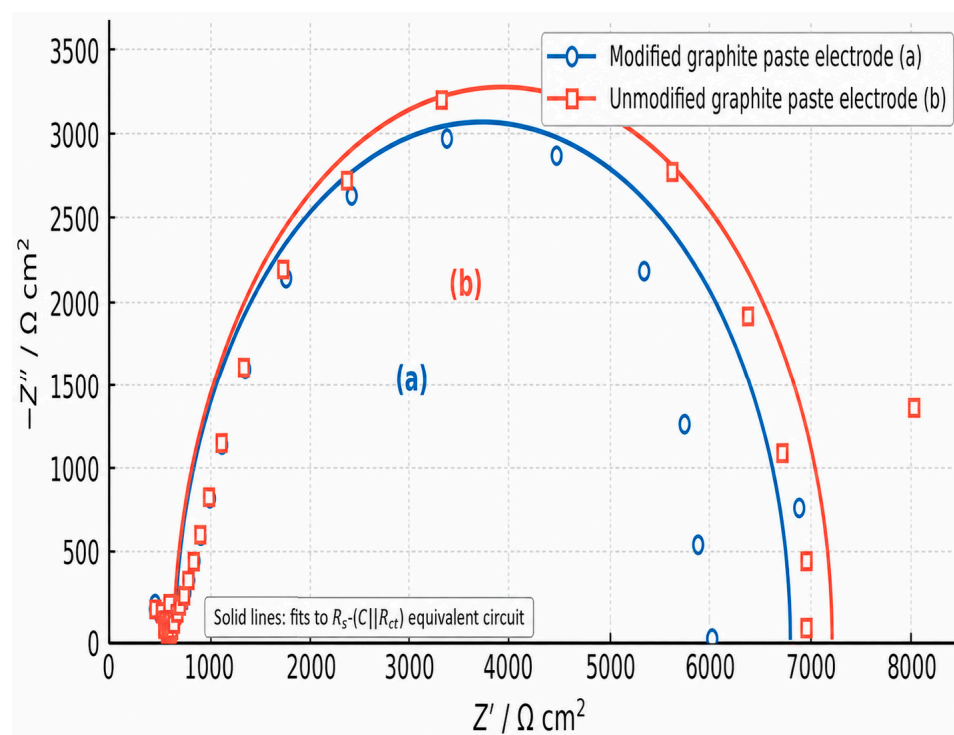


Figure 5. Nyquist plots obtained for the modified graphite paste electrode (a) and the unmodified graphite paste electrode (b) recorded in a solution containing $5.0\text{ mol}\cdot\text{L}^{-1}$ $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ and $0.10\text{ mol}\cdot\text{L}^{-1}$ KCl as the supporting electrolyte at open-circuit potential (OCP = 0.175 V). The solid lines represent fits to the $R_s-(C||R_{ct})$ equivalent circuit.

As shown in Figure 5, both electrodes display well-defined semicircular arcs in the Nyquist plot, characteristic of a charge-transfer-controlled interfacial process. The diameter of each semicircle corresponds directly to the charge-transfer resistance (R_{ct}) at the electrode–electrolyte interface. A clear difference between the two electrodes is observed: the unmodified graphite paste electrode (curve b) exhibits a significantly larger semicircle, while the modified electrode (curve a) shows a markedly reduced arc diameter, indicating improved interfacial charge-transfer kinetics upon surface modification.

Although the decrease in R_{ct} is moderate, it is consistent with the significant increase in electroactive surface area and improved mass transport. The impedance data were fitted using an R_s –($C\parallel R_{ct}$) equivalent circuit, where R_s represents the solution resistance, C is the interfacial capacitance, and R_{ct} is the charge-transfer resistance. This equivalent circuit was selected as the simplest model consistent with the observed single semicircular response, which is characteristic of a one-time-constant interfacial process. The fitted parameters for both electrodes are summarized in Table S2.

The straight line in the low-frequency region corresponds to Warburg impedance, confirming diffusion-controlled mass transport. The quality of the equivalent circuit fitting was evaluated based on the relative residuals of the impedance data. For the unmodified graphite paste electrode, the relative residual did not exceed 5%, confirming excellent agreement between the fitted model and the experimental data. For the modified electrode, the residual remained below 10%, which is fully acceptable in EIS analysis and reflects the fact that the experimental frequency window did not encompass the complete low-frequency arc of the modified electrode, thereby limiting the precision of the R_{ct} determination. In both cases, the selected R_s –($C\parallel R_{ct}$) equivalent circuit model is validated by the good overall agreement with the experimental Nyquist plots.

The R_s values obtained for both electrodes are nearly identical (617.2 and 613.3 $\Omega\cdot\text{cm}^2$, respectively), confirming that the ohmic contribution of the electrolyte solution remained essentially unchanged during the measurements, and that any observed differences in impedance response arise solely from changes at the electrode surface.

The decrease in R_{ct} from 6569 $\Omega\cdot\text{cm}^2$ (unmodified) to 6145 $\Omega\cdot\text{cm}^2$ (modified) corresponds to a decrease of approximately 6.5%, confirming that the incorporation of 5-(4-Aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione into the graphite paste matrix improves the interfacial electron-transfer properties of the electrode. It should be noted that a modest R_{ct} reduction is fully consistent with the nature of this modification: the N,S-donor ligand acts primarily as a preconcentration agent for Cu(II) rather than as a highly conductive surface layer. The principal benefit of modification is the introduction of additional electroactive coordination sites at the electrode surface, which facilitates selective Cu(II) binding and subsequent electrochemical reduction, rather than a dramatic enhancement of bulk electron-transfer kinetics. This interpretation is further supported by the nearly twofold increase in electroactive surface area (0.065 cm^2 vs. geometric 0.0314 cm^2) and the Warburg coefficient $W_o\text{-P} = 0.51 \approx 0.5$, both of which confirm that the dominant improvement upon modification is in mass transport and surface accessibility rather than in charge-transfer rate.

These EIS results are consistent with the cyclic voltammetry data presented in Table S2, collectively confirming the improved electrochemical activity of the modified graphite paste electrode.

3.1.2. SEM Analysis of the Modified Graphite Electrode

The SEM images reveal that the electrode surface possesses a well-developed and heterogeneous morphology. At the same time, the uniform distribution of active sites and the absence of large agglomerates indicate good interparticle contact and confirm the ef-

fectiveness of the surface modification process. These morphological features are consistent with the cyclic voltammetry results and suggest that the electrochemical activity of the modified graphite electrode (MGE) is closely associated with its developed surface structure, as illustrated in Figure 6.

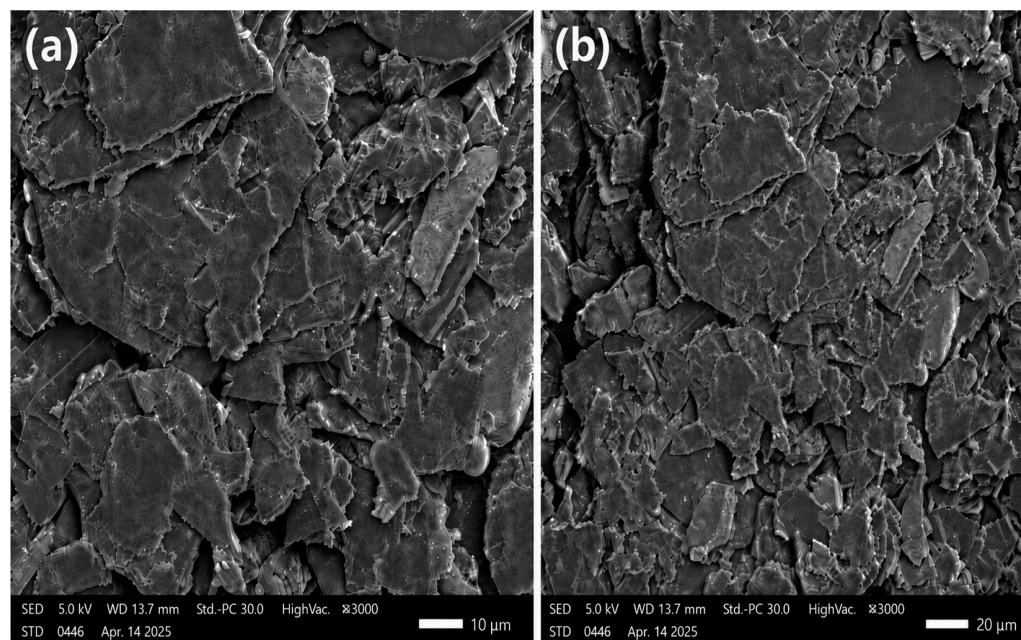


Figure 6. SEM images of the modified electrode (a) $\times 1000$ and (b) $\times 550$. Scale bar: (a) $10\ \mu\text{m}$ and $20\ \mu\text{m}$ (b). The SEM images reveal a rough, porous and layered morphology, which increases the effective surface area and facilitates electron transfer.

The presence of interparticle voids enhances mass transport of Cu(II) ions to the electrode surface. Furthermore, the SEM micrographs demonstrate that the electrode surface is composed of plate-like (layered) graphite particles. The lateral dimensions of these particles are mainly in the range of $5\text{--}20\ \mu\text{m}$, while some larger plates reach approximately $25\text{--}40\ \mu\text{m}$. The particles exhibit angular and irregular shapes, and the surface contains fine cracks and lamellar features and partial edge separation of graphite plates. Large agglomerates were not observed, whereas interparticle gaps of about $0.5\text{--}3\ \mu\text{m}$ are present between the plates. Such a structure provides an enlarged active surface area and promotes efficient particle-to-particle electrical contact.

3.2. Effect of pH on the Analytical Signal

Cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of Cu(II) ions at the surface of the modified graphite electrode (MGE), enabling evaluation of both charge-transfer characteristics and reaction reversibility [18,19]. The influence of supporting electrolyte composition and pH is critical, as it affects not only the kinetics of electron transfer but also the chemical speciation of metal ions in the solution.

The electrochemical reduction of Cu(II) has been reported to depend strongly on pH and the nature of the supporting electrolyte [20,21]. At low pH values, Cu(II) remains fully soluble and electroactive, whereas at pH values above 5.75, precipitation of Cu(OH)_2 occurs, limiting its participation in electrode processes [22]. Therefore, sulfuric acid solutions with concentrations of 0.1 , 0.01 , and $0.001\ \text{mol}\cdot\text{L}^{-1}$ (corresponding to pH $1.0\text{--}3.5$) were selected as supporting electrolytes, and pH values were measured using a calibrated pH meter (accuracy ± 0.05 pH units). The corresponding CV curves are presented in Figure 7.

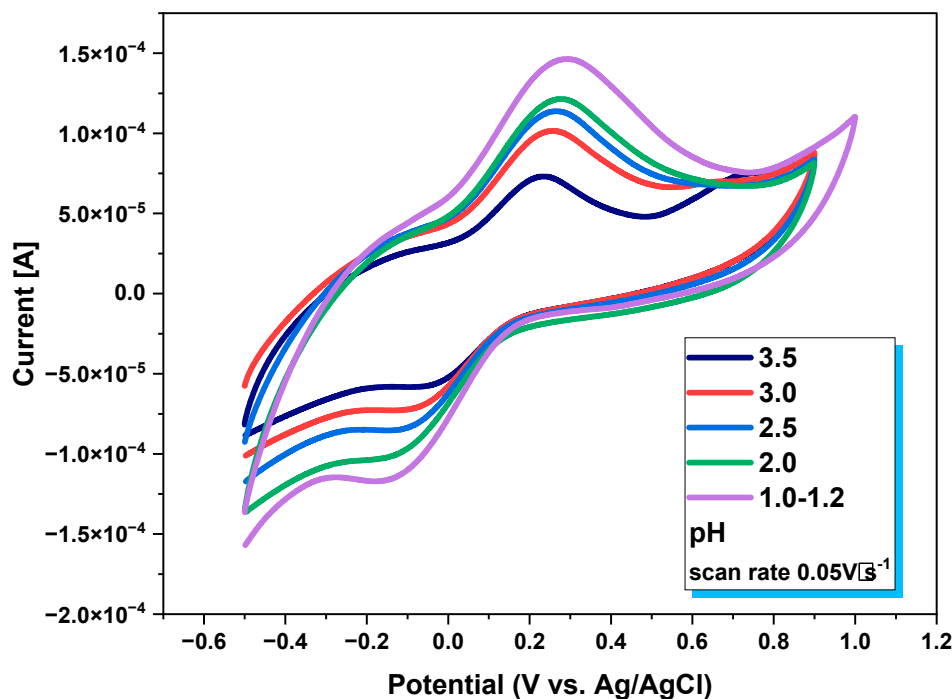


Figure 7. Effect of pH on the cyclic voltammetric response of Cu(II) at the modified graphite electrode (MGE). Experimental conditions: Cu(II) concentration $0.1 \mu\text{mol}\cdot\text{L}^{-1}$; supporting electrolyte H_2SO_4 ($0.001\text{--}0.1 \text{ mol}\cdot\text{L}^{-1}$, pH 1.0–3.5); scan rate $0.05 \text{ V}\cdot\text{s}^{-1}$; temperature 298 K.

As shown in Figures 7 and 8, decreasing pH leads to a significant increase in both anodic and cathodic peak currents. This enhancement is primarily attributed to the increased availability of electroactive Cu(II) ions in strongly acidic media and the suppression of $\text{Cu}(\text{OH})_2$ formation, which facilitates mass transport of Cu(II) species toward the electrode surface. The linear relationship between I_{pa} and pH ($R^2 = 0.963$, Figure 8), with peak current decreasing as pH increases, confirms that pH exerts a systematic and reproducible influence on the analytical signal.

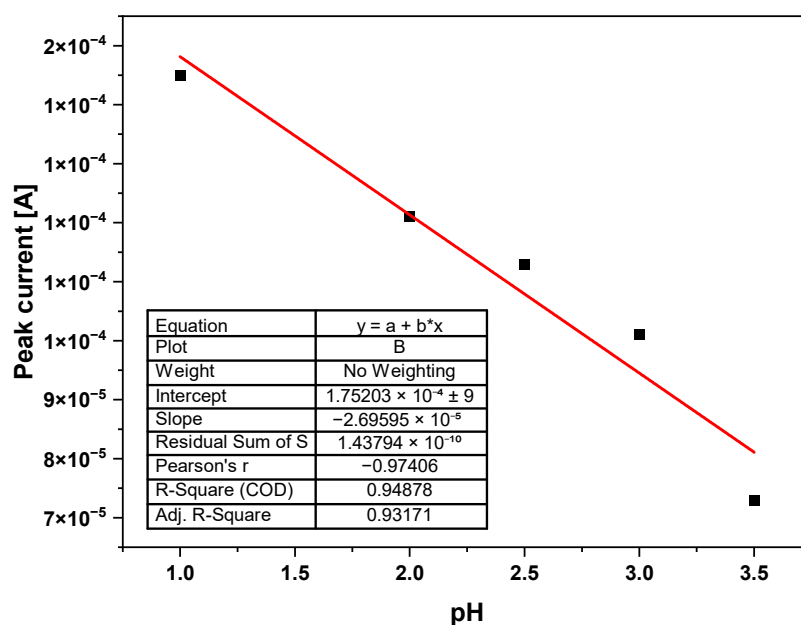


Figure 8. Effect of pH on the anodic peak current (I_{pa}).

It should be noted that the increase in peak current at lower pH reflects improved mass transport and Cu(II) chemical speciation, rather than enhanced electron transfer kinetics. On the contrary, the cathodic peak potential shifted toward more negative values with decreasing pH, indicating increased overpotential and kinetically less favorable electron transfer under highly acidic conditions. These two effects must be interpreted independently: peak current is governed by the chemical availability of Cu(II) in solution, while peak potential reflects kinetic constraints at the electrode–electrolyte interface. This behavior is consistent with the quasi-reversible nature of the Cu(II)/Cu(0) process at the MGE surface, as further discussed in Section 3.3.

To further investigate this point, additional CV measurements were performed using an ammonia buffer as the supporting electrolyte at higher pH values. Under these conditions, no significant change in the Cu(II) analytical signal was observed compared with the strongly acidic medium; neither the peak current nor its reproducibility improved. Accordingly, the strongly acidic H₂SO₄ medium (pH 1.0–2.0) was retained as the optimal supporting electrolyte for the proposed method (Figure S1).

3.3. Effect of Scan Rate

The electrochemical behavior of Cu(II) ions at the surface of the modified graphite electrode (MGE) was investigated at different scan rates using cyclic voltammetry. The voltammograms recorded in the scan rate range of 0.03–0.10 V·s^{−1} (Figure 7) exhibit well-defined anodic and cathodic peaks corresponding to the Cu(II)/Cu(0) redox couple. As the scan rate increased, both anodic and cathodic peak currents increased proportionally, indicating enhanced mass transport. Specifically, the anodic peak current (*I*_{pa}) increased from 1.07×10^{-4} A to 1.85×10^{-4} A, while the cathodic peak current (*I*_{pc}) increased from 8.5×10^{-5} A to 1.44×10^{-4} A (Table 1).

The nature of the electrode process was evaluated based on the peak potential separation (ΔE_p), the *I*_{pa}/*I*_{pc} ratio, and the dependence of peak current on the square root of scan rate. The observed ΔE_p values (110–150 mV) significantly exceed those expected for an ideal reversible electrochemical system.

The large ΔE_p values indicate a pronounced deviation from ideal reversible behavior. Although a theoretical ΔE_p of ~29.5 mV is often cited for a two-electron reversible process, the electrochemical reduction of Cu(II) in the presence of coordinating ligands is known to proceed via multi-step pathways ($\text{Cu}^{2+} \rightarrow \text{Cu}^+ \rightarrow \text{Cu}^0$) and is frequently accompanied by kinetic limitations associated with electron transfer and structural reorganization of the coordination sphere. Therefore, direct comparison with the ideal Nernstian value is not strictly applicable in this system. The observed behavior is thus characteristic of a quasi-reversible electrochemical process, in which the electron transfer rate is finite and comparable to the timescale of the experiment [23].

Furthermore, the linear dependence of peak current on the square root of scan rate ($I_p \propto v^{1/2}$) confirms that the electrochemical process is predominantly diffusion-controlled.

With increasing scan rate, the anodic peak potential (*E*_{pa}) shifted from 0.25 V to 0.35 V, while the cathodic peak potential (*E*_{pc}) shifted from 0.14 V to 0.20 V. Such shifts are typical for quasi-reversible systems and reflect kinetic limitations in the electron transfer step. The half-wave potential, calculated as $E_{1/2} = (E_{pa} + E_{pc})/2$, remained within the range of 0.225–0.275 V, indicating that the thermodynamic properties of the redox couple are relatively stable despite kinetic constraints (Figure 9).

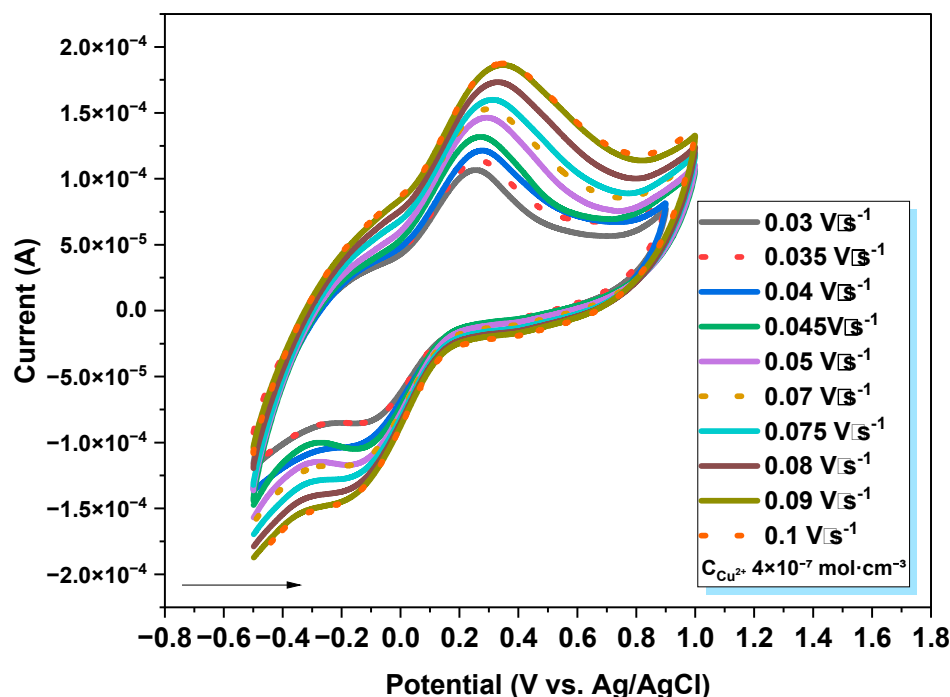


Figure 9. Cyclic voltammograms of Cu(II) at the MGE surface at scan rates from 0.03 to 0.10 V·s^{−1}. Supporting electrolyte: H₂SO₄ (pH 1.0); T = 298 K.

Table 1. Cyclic voltammetry parameters of Cu(II) at the MGE surface at scan rates from 0.03 to 0.10 V·s^{−1}. T = 298 K; A = 0.065 cm²; n = 2; C = 4.0 μMol·L^{−1}. E_{1/2} = (E_{pa} + E_{pc})/2.

v (V·s ^{−1})	√v	E _{pa} (V)	E _{pc} (V)	ΔE _p (mV)	E _{1/2} (V)	I _{pa} (A)	I _{pc} (A)	I _{pa} /I _{pc}
0.03	0.173	0.25	0.14	110	0.195	1.07 × 10 ^{−4}	8.5 × 10 ^{−5}	1.26
0.035	0.187	0.26	0.14	120	0.200	1.14 × 10 ^{−4}	8.5 × 10 ^{−5}	1.34
0.04	0.2	0.28	0.15	130	0.215	1.22 × 10 ^{−4}	1.02 × 10 ^{−4}	1.196
0.045	0.212	0.29	0.16	130	0.225	1.32 × 10 ^{−4}	1.03 × 10 ^{−4}	1.28
0.05	0.2236	0.29	0.16	130	0.225	1.45 × 10 ^{−4}	1.15 × 10 ^{−4}	1.26
0.06	0.2449	0.31	0.18	130	0.245	1.52 × 10 ^{−4}	1.16 × 10 ^{−4}	1.31
0.07	0.2646	0.32	0.19	130	0.255	1.62 × 10 ^{−4}	1.26 × 10 ^{−4}	1.29
0.08	0.2828	0.35	0.20	150	0.275	1.72 × 10 ^{−4}	1.36 × 10 ^{−4}	1.26
0.09	0.3000	0.35	0.20	150	0.275	1.85 × 10 ^{−4}	1.42 × 10 ^{−4}	1.30
0.10	0.3162	0.35	0.20	150	0.275	1.85 × 10 ^{−4}	1.44 × 10 ^{−4}	1.29

To further distinguish between diffusion-controlled and adsorption-controlled processes, the relationship between log(I_p) and log(v) was analyzed. For a diffusion-controlled process, the slope of the log(I_p) vs. log(v) plot is theoretically equal to 0.5, whereas a slope of 1.0 indicates adsorption control. The experimental slopes obtained were 0.48 (anodic) and 0.51 (cathodic), both close to the theoretical value of 0.5, confirming semi-infinite linear diffusion.

A linear relationship between peak current and the square root of scan rate (v^{1/2}) was also observed (Figure 10), with correlation coefficients R² = 0.983 and R² = 0.966 for anodic and cathodic processes, respectively. The corresponding regression equations are

$$I_{pa} = 5.738 \cdot v^{1/2} + 0.3678 \quad (R^2 = 0.983)$$

$$I_{pc} = 4.335 \cdot v^{1/2} + 0.3193 \quad (R^2 = 0.966)$$

It should be noted that the Randles–Ševčík equation is strictly valid only for fully reversible systems. Given the quasi-reversible nature of the Cu(II)/Cu(0) process at the MGE surface, the calculation of a diffusion coefficient would yield only an apparent value and cannot be considered a reliable intrinsic parameter. Therefore, no diffusion coefficient is reported in this study. The linear I_p – $v^{1/2}$ relationship is considered sufficient evidence that mass transport is governed by semi-infinite linear diffusion under the investigated conditions [24,25].

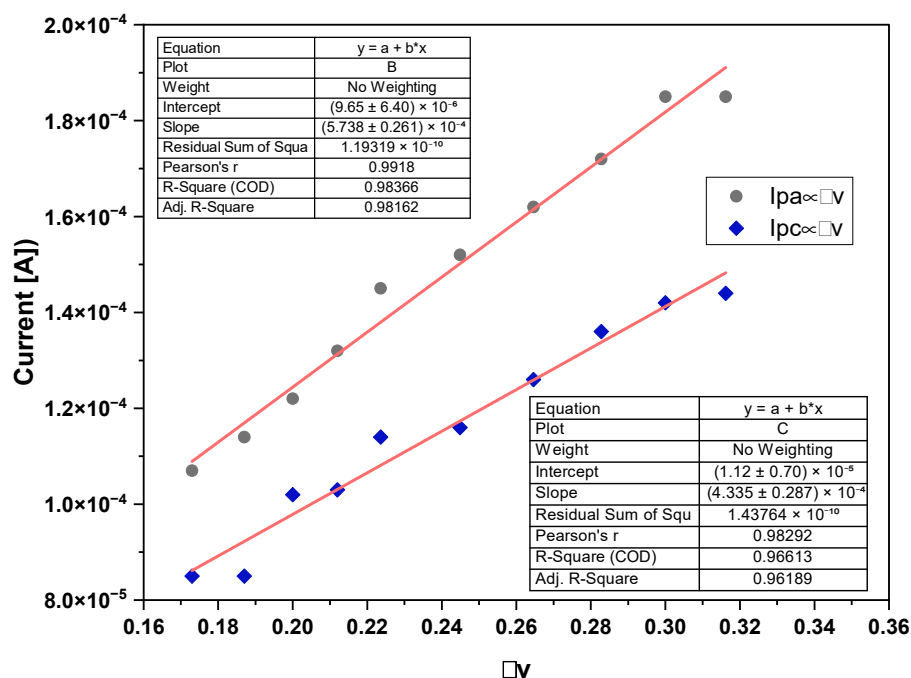


Figure 10. Linear dependence of anodic (I_{pa}) and cathodic (I_{pc}) peak currents on the square root of scan rate ($v^{1/2}$) for Cu(II) at the MGE surface. For comparative evaluation, cyclic voltammograms of Cu(II) ions were recorded at various scan rates using the unmodified graphite electrode, and the obtained results are presented in Figure S2.

3.4. Differential Pulse Voltammetric Analysis of Copper Ions in Solution

In the absence of Cu(II) ions, no measurable change in current response was observed under otherwise identical experimental conditions; the blank voltammogram remained featureless within the investigated potential window, consistent with the results obtained for the modifier alone (Section 2.4). This confirms that the peak current changes described below arise specifically from the presence of Cu(II) ions rather than from the background electrolyte or the modifier itself Figure S3.

Differential pulse voltammetry (DPV) was employed to determine the concentration of Cu(II) ions using the modified graphite electrode. This technique is highly effective for detecting substances at very low concentrations. The electrochemical behavior of the Cu(II)/Cu(0) redox couple was investigated by DPV, as illustrated in Figure 11.

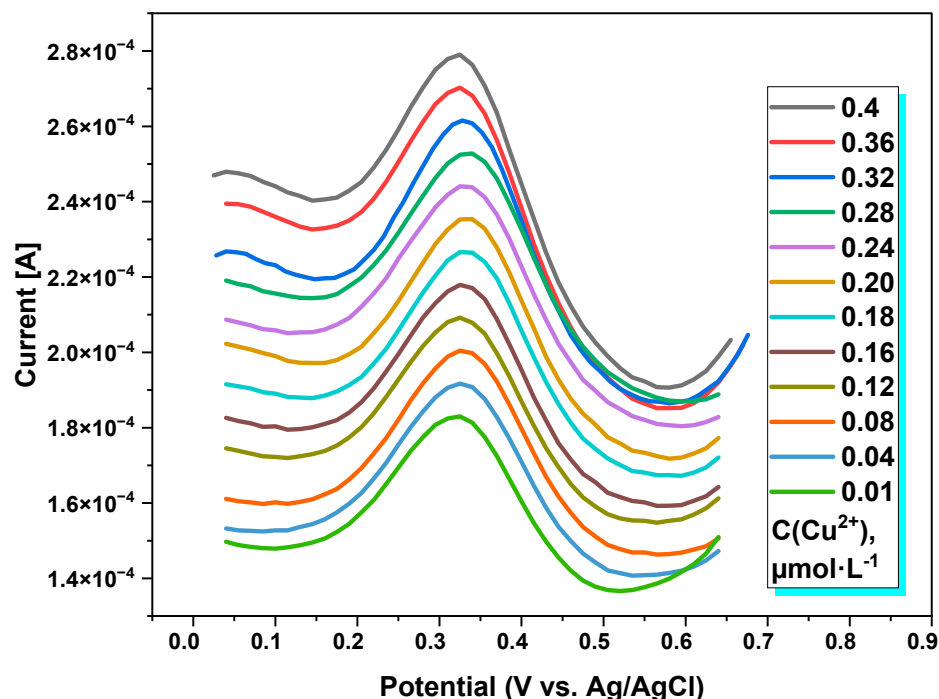


Figure 11. Differential pulse voltammograms of Cu^{2+} ions recorded at the MGE for different concentrations. Conditions: $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$, pulse amplitude 50 mV, pulse width 50 ms, step potential 5 mV, accumulation time 60 s, $T = 298 \text{ K}$. (The blank signal and the Cu(II) -dependent voltammetric response were compared under identical conditions, as presented in Figure S4).

Prior to extracting the peak current values used for quantitative analysis, a baseline correction was applied to each DPV voltammogram to eliminate the background (charging) current contribution and to ensure accurate and reproducible determination of the net analytical (Faradaic) peak current. The same baseline-correction procedure was subsequently used to obtain the peak current values plotted in the Cu(II) calibration curve.

The DPV results (Figure 11) showed that the analytical signal increased progressively with increasing Cu(II) ion concentration in the range of $0.01\text{--}0.4 \mu\text{mol}\cdot\text{L}^{-1}$, which fully encompasses the Cu(II) concentration detected in the Aydar–Arnasoy reservoir water ($0.0944 \mu\text{M}$). The selected concentration window was deliberately optimised for trace-level environmental monitoring and remains substantially below the WHO guideline value for copper in drinking water (2 mg L^{-1} , $\approx 31.5 \mu\text{mol}\cdot\text{L}^{-1}$). The peak current increased from $183 \mu\text{A}$ to $279 \mu\text{A}$, indicating a well-defined linear relationship between Cu(II) concentration and the current response ($R^2 = 0.99507$). In all voltammograms, the main peak appeared at $\sim 0.322 \text{ V}$, and its invariant position confirms the reproducibility of the electrochemical process at the modified electrode surface. The systematic increase in peak height with increasing Cu(II) concentration demonstrates the high sensitivity of the modified graphite electrode. These results confirm that the DPV method provides reliable and quantitative determination of Cu(II) ions at environmentally relevant sub-micromolar concentrations.

Based on these results, the regression analysis was performed over twelve calibration points in the concentration range of $0.01\text{--}0.40 \mu\text{mol}\cdot\text{L}^{-1}$, yielding the following calibration equation: $I_p (\mu\text{A}) = 252.05C + 180.42$ with a correlation coefficient of ($R^2 = 0.99507$), confirming excellent linearity within the investigated concentration range. The corresponding calibration plot is presented in Figure 12.

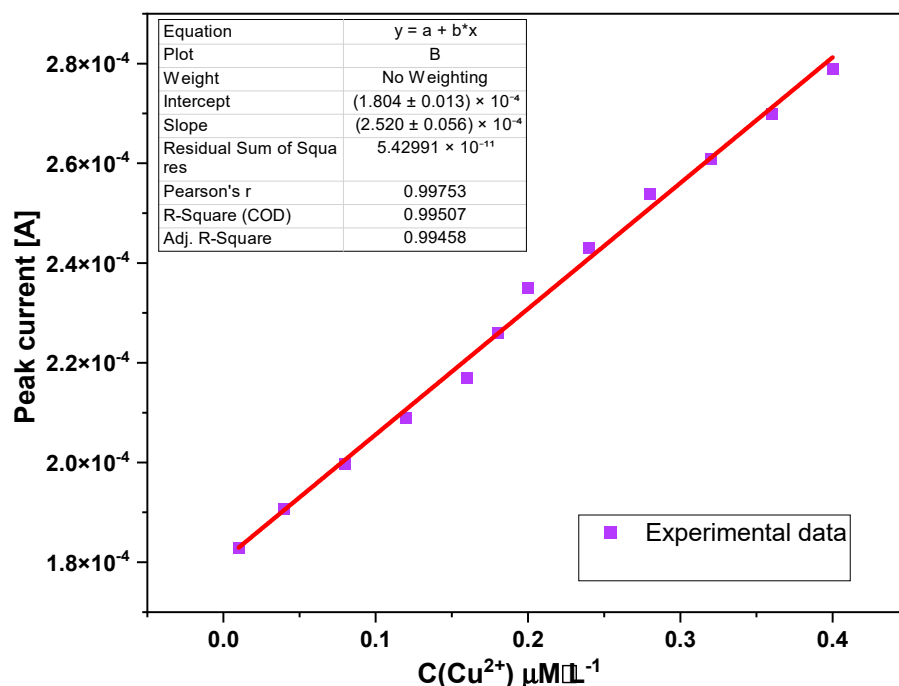


Figure 12. Linear calibration curve for Cu(II) determination: dependence of peak current (I_p) on Cu(II) concentration in the range 0.01–0.4 $\mu\text{mol}\cdot\text{L}^{-1}$ ($R^2 = 0.99507$; supporting electrolyte: 0.1 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4).

The linear response confirms the suitability of the developed DPV method for quantitative Cu(II) determination within the investigated concentration range. The limits of detection and quantification were calculated using the following Equations (2) and (3).

$$\text{LOD} = 3.3\sigma/S \quad (2)$$

$$\text{LOQ} = 10\sigma/S \quad (3)$$

The obtained values, $\text{LOD} = 0.02 \mu\text{mol}\cdot\text{L}^{-1}$ and $\text{LOQ} = 0.06 \mu\text{mol}\cdot\text{L}^{-1}$, are well below the Cu(II) concentration found in the Aydar–Arnasoy reservoir water ($0.0944 \mu\text{mol}\cdot\text{L}^{-1}$) and significantly lower than the WHO guideline value for copper in drinking water (2 mg L^{-1} , $\approx 31.5 \mu\text{mol}\cdot\text{L}^{-1}$). These values confirm that the developed method possesses sufficient sensitivity for reliable detection of Cu(II) at environmentally relevant concentrations without the need for additional preconcentration steps. The LOD achieved in the present work is appropriate for environmental monitoring purposes where the target analyte concentration typically falls in the range of 0.01–0.5 $\mu\text{mol}\cdot\text{L}^{-1}$. It should be noted that, unlike several nanomaterial-based sensors reported in the literature (Table 4), the present electrode does not employ a dedicated preconcentration stage beyond the 60 s accumulation step; extending the accumulation time or optimising the pulse parameters is expected to further lower the detection limit in future studies. The analytical parameters of the proposed MGE, including the linear range and detection limit, were compared with those of previously reported modified graphite electrode-based sensors for Cu(II) determination, as shown in Table 2.

Table 2. Comparison of the analytical performance of the proposed MGE with previously reported modified electrodes for voltammetric determination of Cu(II).

No	Method	Electrode Material	Supporting Electrolyte	Complexing Reagent for Cu(II)	Linear Range	LOD	Analyzed Matrices
[26]	DPV	PGE/PPy/Cyanex 921 modified pencil graphite electrode	BR buffer, pH 3.0 + 0.1 M LiClO ₄	Cyanex 921 incorporated into the PPy-modified electrode	20–140 ppm	2.15 ppm	Spiked water samples
[27]	Voltammetric determination/stripping response	Carbon paste electrode modified with Fe ₃ O ₄ /eggshell nanocomposite and carbon nanotubes	0.2 M HCl	Fe ₃ O ₄ /eggshell nanocomposite acts as the modifier/preconcentration phase; no separate solution-phase ligand	0.5–310 ng mL ⁻¹	0.033 ng mL ⁻¹	Drinking water, wastewater, hair samples, certified reference materials
[28]	DPSV	CPE modified with 1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol, CPE/BT	Britton–Robinson buffer, pH 5.00	1,3-bis(4-butyl-1H-1,2,3-triazol-1-yl)propan-2-ol immobilized in CPE	1.00×10^{-8} – 1.30×10^{-7} mol L ⁻¹	1.67×10^{-9} mol L ⁻¹	Cabbage cultivated with Bordeaux syrup
[29]	SWV after open-circuit adsorption/pre-concentration	Maize tassel-modified carbon paste electrode, MT-CPE	0.05 M NaNO ₃ , pH 5.0	Maize tassel biomass functional groups; no separate complexing reagent	1.23 µM–0.4 mM	0.13 ± 0.01 µM	Tap water samples
[30]	Voltammetric sensor with extraction–washing–measurement steps	Molecularly imprinted polymer-modified carbon paste electrode, MIP-CP	Not specified in accessible abstract	Cu(II)-selective molecularly imprinted polymer incorporated into CPE	7.0×10^{-8} – 1.0×10^{-6} mol L ⁻¹ ; 1.0×10^{-6} – 1.0×10^{-4} mol L ⁻¹	2.3×10^{-8} mol L ⁻¹	Yellow River water
[31]	ASV	In situ antimony film-coated carbon paste electrode, SbF-CPE	0.01 M HCl	Procedure 1: none; Procedure 2: Pyrocatechol Violet, PCV	Up to 120 ppb without PCV; up to 100 ppb with PCV	1.45 ppb without PCV; 1.10 ppb with PCV	River water; compared with ICP-MS
[32]	DPV with open-circuit preconcentration and subsequent ASV	Montmorillonite-modified carbon paste electrode	Not specified in accessible abstract	Montmorillonite clay modifier; ion-exchange/preconcentration phase	4×10^{-8} – 8×10^{-7} mol L ⁻¹	4×10^{-8} mol L ⁻¹	Model aqueous solutions; humic ligand and interference studied
This work	CV and DPV	Graphite paste electrode modified with N,S-donor triazole–thione ligand	0.1 mol·L ⁻¹ H ₂ SO ₄ (pH 1.0–1.2)	5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione	0.01–0.4	0.02	Reservoir water (Aydar–Arnasoy)

3.5. Effect of Interfering Ions on the Accuracy and Repeatability of the Voltammetric Determination of Cu(II)

To evaluate the selectivity of the developed voltammetric method, the influence of various ions that may be present in the solution on the Cu^{2+} signal was investigated Table 3 For this purpose, an electrochemical cell of 25 mL volume was prepared by adding 2.0 mL of 0.1 M sulfuric acid as the supporting electrolyte and $1 \mu\text{mol}\cdot\text{L}^{-1}$ Cu(II) standard solution. Thereafter, different metal ions were introduced into the solution at defined ratios relative to Cu^{2+} . Specifically, the following ratios were applied: Pb^{2+} —1:0.50, Cd^{2+} —1:2.00, Zn^{2+} —1:20, Hg^{2+} —1:0.10, Fe^{3+} —1:1.00, Ni^{2+} —1:10, Co^{2+} —1:5, Al^{3+} —1:5, and Mn^{2+} —1:5. Strong complexing ligands such as CN^- and EDTA^{4-} were also added at ratios of 1:0.10 and 1:0.05, respectively. After all components were mixed, the total volume of the solution was adjusted to 25 mL with bidistilled water.

Table 3. Effect of Interfering ions on the accuracy and repeatability of the voltammetric determination of Cu(II).

Interfering Ion	Added Ion C_x ($\mu\text{mol L}^{-1}$)	$\text{Cu}^{2+}:\text{X}$ Ratio	Found Cu^{2+} , $\mu\text{mol L}^{-1}$ ($\bar{X} \pm \Delta X$)	<i>n</i>	S	Sr
Blank	0	—	1.000 ± 0.003	5	0.0024	0.002
Pb^{2+}	0.50	1:0.50	0.942 ± 0.006	5	0.0050	0.005
Cd^{2+}	2.0	1:2.00	0.965 ± 0.008	5	0.0066	0.007
Zn^{2+}	20.0	1:20	0.981 ± 0.005	5	0.0041	0.004
Hg^{2+}	0.10	1:0.10	0.910 ± 0.012	5	0.0100	0.011
Fe^{3+}	1.00	1:1.00	0.925 ± 0.010	5	0.0084	0.009
Ni^{2+}	10.0	1:10	0.955 ± 0.007	5	0.0060	0.006
Co^{2+}	5.0	1:5	0.982 ± 0.004	5	0.0033	0.003
Al^{3+}	5.0	1:5	0.990 ± 0.005	5	0.0042	0.004
Mn^{2+}	5.0	1:5	0.987 ± 0.006	5	0.0050	0.005
CN^-	0.10	1:0.10	0.210 ± 0.020	5	0.0165	0.078
EDTA^{4-}	0.05	1:0.05	0.050 ± 0.010	5	0.0083	0.167

The presence of Zn^{2+} , Mn^{2+} , Co^{2+} , and Al^{3+} ions exhibited almost no influence on the analytical signal, with recovery values remaining close to 100%, confirming that these ions do not interfere under practical conditions. Ions such as Pb^{2+} , Cd^{2+} , Fe^{3+} , Ni^{2+} , and Hg^{2+} , which are capable of forming complexes or participating in code position processes, caused a moderate decrease in the Cu^{2+} peak height. Nevertheless, the accuracy and repeatability of the determination remained satisfactory, indicating that the method can still be applied reliably in moderately contaminated matrices.

The strongest interference was observed from CN^- and EDTA^{4-} , which significantly reduced the concentration of free Cu^{2+} due to strong complex formation, thereby disrupting the stability of the electrochemical response. In such cases, additional sample pretreatment or the use of masking agents becomes necessary.

Overall, the obtained results demonstrate that the developed voltammetric method operates reliably in the presence of common inorganic ions, whereas systems containing strong complexing ligands require supplementary preparation steps. Owing to its high sensitivity and minimal susceptibility to interfering ions, the method is well-suited for the analysis of natural samples containing Cu(II) and is recommended for practical application.

3.6. Electrode Reusability and Operational Stability

The operational stability and reusability of the modified graphite paste electrode were evaluated through repeated differential pulse voltammetric measurements of a $0.10 \mu\text{mol}\cdot\text{L}^{-1}$ Cu(II) solution under the optimized experimental conditions. After each measurement, the electrode surface was rinsed with distilled water and lightly polished before reuse. (See Table 4).

The electrode exhibited good repeatability over 30 consecutive measurements, retaining approximately 93% of its initial current response. The relative standard deviation (RSD) of the peak current did not exceed 4.2%, indicating satisfactory operational stability and reproducibility.

In addition, the storage stability of the modified electrode was investigated by storing the electrode at room temperature in a dry environment. After 14 days of storage, the electrode retained approximately 91% of its original response toward Cu(II), demonstrating acceptable long-term stability of the modifier within the graphite paste matrix.

These results confirm that the proposed electrode can be reused multiple times without significant loss of analytical performance, making it suitable for routine environmental monitoring applications.

Table 4. Comparison of electrochemical methods for copper(II) detection.

No	Method	Electrode Material	Supporting Electrolyte	Complexing Reagent for Cu(II)	Linear Range	LOD	Analyzed Matrices
[33]	CV and DPASV	Modified GCE	$0.1 \text{ mol}\cdot\text{L}^{-1}$ HAc-NaAc (pH 4.5)	RGO-chitosan/poly-L-lysine nanocomposite	$0.05\text{--}10.0 \mu\text{g/L}$	$0.02 \mu\text{g/L}$	Drinking water
[34]	Voltammetry	Modified graphite sensor	100 mg/dm^3 Au(III) solution	Diazonium salts	$0.8\text{--}3200.0 \mu\text{g/L}$	$0.2 \mu\text{g/L}$	Human hair
[35]	ASV	Diamond/graphite nanoplatelets electrode	$0.1 \text{ mol}\cdot\text{L}^{-1}$ acetate buffer	—	$10\text{--}250 \mu\text{g/L}$	$0.45 \mu\text{g/L}$	Environmental samples
[36]	DPASV	Modified GCE	Acetate buffer	CeO ₂ nanoparticle-decorated graphene hybrid	$0.2\text{--}2.5 \mu\text{M}$	$0.1636 \mu\text{M}$	Aqueous/wastewater
[37]	DPV	Stainless steel electrode	$0.5 \text{ M H}_2\text{SO}_4$	EDTA_PANI/SWCNTs nanocomposite	$1.2 \mu\text{M}$ to 2 mM	$0.08 \mu\text{M}$	Environmental samples
[38]	CV and DPV	Modified GCE	BR buffer	poly-5NP and poly-5A6NP	$1.0 \times 10^{-2}\text{--}1.0 \times 10^{-12} \text{ M}$	poly-5A6NP/GC $0.8 \times 10^{-10} \text{ M}$ poly-5NP/GC $0.2 \times 10^{-10} \text{ M}$	Environmental samples
[39]	CV	Glassy carbon electrode	Acetate buffer	Lysine amino acid	$0.001\text{--}0.006 \text{ M}$	$8 \times 10^{-6} \text{ M}$	Aqueous medium
[40]	CV and SWV	Static Mercury Electrode (SME)	Acetic acid/NaOH	Cephalosporin antibiotics (CEX, CEP, CML, CRX, CTX, CFZ)	—	$7 \times 10^{-10} \text{ M}$	Pharmaceutical samples
[41]	DPASV	Hanging Mercury Drop Electrode (HMDE)	pH 1.5 (HNO_3)	Natural organic ligands from <i>E. crassipes</i>	—	$1.12 \mu\text{g/mL}$	Aqueous plant extract (Nile water)
[42]	CV	Platinum electrode	Ethyl alcohol/acetic acid/DMFA	5-(o-aminophenyl)-1,3,4-oxadiazole-2-thione	$0.1\text{--}50 \text{ nM}$	0.061 nM	Industrial process water (Almalyk)
[43]	EIS	Graphene oxide (Au electrode)	Phosphate buffer	Rhodamine B hydrazide (RBH)	$0.1\text{--}50 \text{ nM}$	0.061 nM	Aqueous solutions
This work	CV and DPV	Graphite paste electrode modified with N,S-donor	$0.1 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 (pH 1.0–1.2)	5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione	$0.01\text{--}0.4$	0.02	Reservoir water (Aydar–Arnasoy)

triazole–thione
ligand

Abbreviations: CV, cyclic voltammetry; DPV, differential pulse voltammetry; DPASV, differential pulse anodic stripping voltammetry; ASV, anodic stripping voltammetry; SWV, square wave voltammetry; EIS, electrochemical impedance spectroscopy; GCE, glassy carbon electrode; HMDE, hanging mercury drop electrode; SME, static mercury electrode; RGO, reduced graphene oxide; PANI, polyaniline; SWCNTs, single-walled carbon nanotubes; EDTA, ethylenediaminetetraacetic acid; BR, Britton–Robinson buffer; RBH, rhodamine B hydrazide.

3.7. Validation and Application of the Developed Method

The selectivity of the proposed method was confirmed in Section 3.5, where the relative standard deviation (RSD) did not exceed 0.33% across all tested interfering ion systems, indicating a high level of precision and good reproducibility. These results demonstrate that the proposed method can be effectively applied for the determination of Cu(II) ions in natural water matrices containing common inorganic ions. To further assess the applicability and accuracy of the method, the developed procedure was applied to the determination of Cu(II) ions in water samples collected from the Aydar–Arnasoy reservoir [19]. For validation purposes, the obtained results were compared with those obtained using inductively coupled plasma optical emission spectrometry (ICP-OES, Avio200 ICP-OES, Perkin Elmer, , Shelton, CT, USA). The elemental composition of the reservoir water determined by ICP-OES analysis is presented in Table 5.

Table 5. Elemental composition of the Aydar–Arnasoy reservoir water determined by ICP-OES analysis (C [$\mu\text{mol}\cdot\text{L}^{-1}$]).

Element	Mg	Cr	As	Li	K	Ca	Fe	Co	Ni	Cu
C [$\mu\text{mol}\cdot\text{L}^{-1}$]	0.1650	0.0769	0.0934	0.288	12.941	34.382	468.26	0.1697	0.1533	0.0944
Element	Zn	Al	B	Se	Sn	Sb	Pb	V	Mo	Cd
C [$\mu\text{mol}\cdot\text{L}^{-1}$]	0.0459	0.0371	20.166	0.671	0.000	0.000	0.2075	0.000	0.6774	0.000

The determination of Cu(II) ions by DPV was carried out as follows. Initially, 2 mL of 0.1 mol·L^{−1} sulfuric acid solution (pH 1.0–1.2) and 23 mL of the reservoir water sample were introduced into the electrochemical cell (Figure 13).

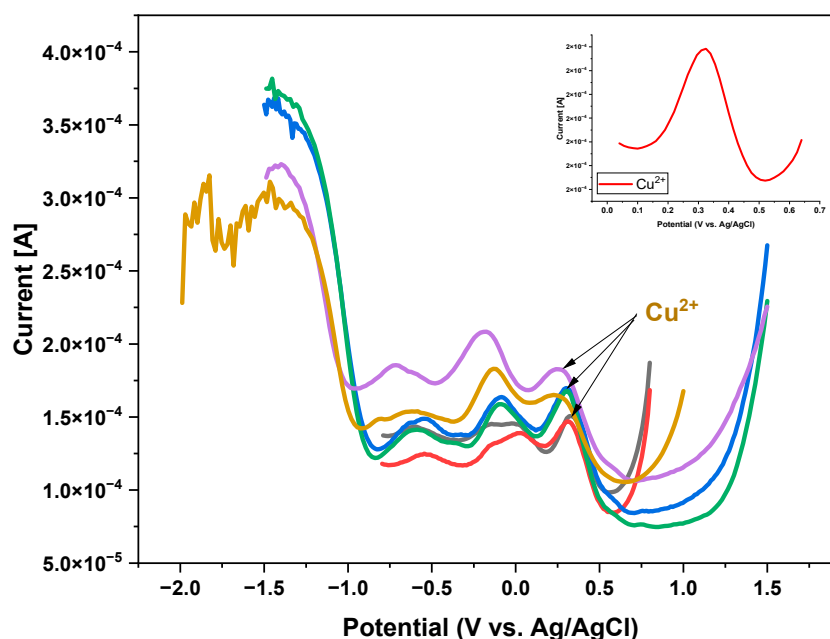


Figure 13. Differential pulse voltammograms obtained for the determination of Cu(II) ions in the Aydar–Arnasoy water sample using the modified graphite electrode (MGE). The inset represents the characteristic Cu(II) peak.

After equilibration, differential pulse voltammograms were recorded under optimized experimental conditions. The analytical results are summarized in Table 6.

The mean concentration of Cu(II) ions determined by the proposed method was $0.0942 \pm 0.0004 \mu\text{mol}\cdot\text{L}^{-1}$ ($p = 0.95$, $n = 5$), with a standard deviation $S = 0.0003$ and a relative standard deviation $S_r = 0.0033$. The calculated Student's t -value was $t_{\text{calc}} = 1.49$, which is lower than the tabulated value $t_{\text{tab}} = 2.776$ at a confidence level of $p = 0.95$ and $n = 5$ (Table 6). This confirms that the difference between the determined and reference values is statistically insignificant, and no systematic error was detected under the applied experimental conditions.

Table 6. Results of DPV determination of Cu(II) in Aydar–Arnasoy reservoir water (reference value by ICP-OES: $C(\text{Cu}^{2+}) = 0.0944 \mu\text{mol}\cdot\text{L}^{-1}$; $n = 5$; $p = 0.95$).

Method	Reference Cu(II) ($\mu\text{mol}\cdot\text{L}^{-1}$)	Found Cu(II) ($\mu\text{mol}\cdot\text{L}^{-1}$) $\bar{X} \pm \Delta X$	n	S	S_r	t_{tab}	t_{calc}
DPV	0.0944	0.0942 ± 0.0004	5	0.0003	0.0033	2.776	1.49

To further confirm the accuracy of the developed method and to evaluate possible matrix effects, a standard addition (spike–recovery) experiment was performed using the same reservoir water sample. Known concentrations of Cu(II) standard solution (0.05 , 0.10 , and $0.15 \mu\text{mol}\cdot\text{L}^{-1}$) were added to aliquots of the sample, and the resulting solutions were analyzed under the optimized DPV conditions. The recovery values ranged from 99.0 to 99.5% , with RSD values below 1.0% ($n = 3$), demonstrating good accuracy, satisfactory precision, and negligible matrix interference (Table 7). These results confirm that the proposed method is suitable for the direct determination of trace Cu(II) ions in reservoir water without additional pretreatment steps.

Table 7. Spike–recovery results for Cu(II) determination in Aydar–Arnasoy reservoir water. $n = 3$; $p = 0.95$.

Sample	Found ($\mu\text{mol}\cdot\text{L}^{-1}$)	Spiked ($\mu\text{mol}\cdot\text{L}^{-1}$)	Total Found ($\mu\text{mol}\cdot\text{L}^{-1}$)	Recovery (%)	RSD (%)
Reservoir water	0.0942	—	—	—	0.33
Spiked 1	0.0942	0.05	0.143 ± 0.001	99.0	<1.0
Spiked 2	0.0942	0.10	0.193 ± 0.001	99.4	<1.0
Spiked 3	0.0942	0.15	0.243 ± 0.001	99.5	<1.0

Overall, the developed electrochemical method possesses high precision, good accuracy, and practical applicability for the determination of trace levels of Cu(II) ions in environmental water samples, representing a reliable and simple alternative to conventional spectrometric techniques.

4. Discussion

Modification of a graphite paste electrode with 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione significantly enhances its electrochemical response toward Cu(II) ions. SEM analysis revealed a heterogeneous, well-developed surface morphology with uniformly distributed active sites, providing an enlarged active surface area (0.065 cm^2 vs. geometric 0.0314 cm^2) and efficient mass transport. For the modified graphite electrode,

the fitted parameters showed $R_{ct} = 6145 \Omega \cdot \text{cm}^2$, $R_s = 613.3 \Omega \cdot \text{cm}^2$ and $W_o\text{-}P = 0.51$, close to the theoretical value of 0.5. This indicates a mainly diffusion-controlled process, consistent with the nearly 45° line in the low-frequency Nyquist region.

It should be noted that the enhanced electrochemical response of the modified electrode likely does not arise solely from N,S-donor coordination-driven preconcentration of Cu(II). The SEM images (Figure 6) reveal a rough, porous, and layered surface morphology, indicating that incorporation of the modifier also increases the physical porosity and effective surface area of the graphite paste matrix. This increase in porosity and roughness contributes to improved analyte mass transport and access to the electrode surface, consistent with the nearly twofold increase in electroactive surface area (0.065 cm^2 vs. geometric 0.0314 cm^2). Therefore, the overall enhancement in analytical signal is most reasonably attributed to a combined effect of surface complexation/preconcentration by the N,S-donor modifier and an increase in surface porosity and roughness, rather than to either factor acting alone.

Compared with nanomaterial-based electrodes reported in the literature (Table 4), the present system offers a considerably simpler fabrication strategy. Graphene/CeO₂ hybrid electrodes [36] and RGO-chitosan/poly-L-lysine composites [33] achieve lower LOD values but require multistep hydrothermal or electropolymerisation procedures that compromise reproducibility. The EDTA-PANI/SWCNTs nanocomposite [37] employs EDC-activated covalent coupling, which adds preparation complexity. It is also worth noting that [42] reported a substantially lower LOD ($0.000061 \mu\text{mol} \cdot \text{L}^{-1}$) for Cu(II) determination using an analogous oxadiazole-thione ligand. However, that method employed a platinum electrode in a non-aqueous ethanol/acetic acid/DMFA medium, which is fundamentally different from the aqueous graphite-paste system developed here. The non-aqueous medium favors a lower background current and reduced competing side reactions, conditions not directly comparable to the aqueous environmental matrices targeted in the present work. Consequently, the LOD difference reflects a difference in operating medium and electrode platform rather than a shortcoming of the N,S-donor coordination mechanism itself. In contrast, the proposed sensor is fabricated by a single-step mixing procedure and achieves an LOD of $0.02 \mu\text{mol} \cdot \text{L}^{-1}$ —significantly lower than the WHO guideline value for copper in drinking water (2 mg L^{-1} , $\approx 31.5 \mu\text{M}$)—which is fully sufficient for environmental monitoring of the Aydar–Arnasoy reservoir, where the measured Cu(II) concentration was $0.0944 \mu\text{mol} \cdot \text{L}^{-1}$.

The use of a small N,S-donor ligand allows a clearer mechanistic interpretation of the sensing process, which is often not possible in complex nanocomposite systems. CV using the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ probe showed increased peak currents and reduced peak-to-peak separation after modification. The linear I_p vs. $\sqrt{v}$ relationship ($R^2 = 0.983$ and 0.966 for anodic and cathodic processes, respectively) validates stable, diffusion-controlled electrochemical behavior. The Cu(II) response was strongly pH-dependent: well-defined redox peaks occurred at pH 1.0–2.0 ($0.1 \mu\text{mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$), while higher pH caused signal suppression via $\text{Cu}(\text{OH})_2$ precipitation.

The detection mechanism involves selective Cu(II) complexation with N,S-donor sites. The modifier undergoes thione–thiol tautomerism, with deprotonated thiolate (S^-) and triazole nitrogen forming a stable N_2S_2 complex that preconcentrates Cu(II) at the surface, followed by reduction: $[\text{Cu}(\text{L})_2] + 2e^- \rightarrow \text{Cu}^0 + 2\text{L}^-$.

DPV achieved LOD = $0.02 \mu\text{mol} \cdot \text{L}^{-1}$ and LOQ = $0.06 \mu\text{mol} \cdot \text{L}^{-1}$ with a linear range of $0.01\text{--}0.4 \mu\text{mol} \cdot \text{L}^{-1}$ ($R^2 = 0.99507$) and a calibration sensitivity of $393.98 \mu\text{A} \cdot \mu\text{M}^{-1}$. Common metal ions (Zn^{2+} , Mn^{2+} , Co^{2+} , Al^{3+} at up to 20-fold excess) caused negligible interference, while Pb^{2+} , Cd^{2+} , Fe^{3+} , Ni^{2+} , and Hg^{2+} produced moderate but acceptable effects on the Cu(II) signal. Strong chelating agents (CN^- , EDTA^{4-}) severely suppressed the signal—an expected outcome that directly confirms the coordination-dependent preconcentration

mechanism: when Cu(II) is fully sequestered in solution by a stronger ligand, it is unavailable for binding at the electrode surface. This behaviour is therefore not a limitation but rather unambiguous mechanistic evidence for the N,S-bidentate coordination mode.

Validation via Aydar–Arnasoy reservoir water analysis yielded results statistically comparable to ICP-OES ($t_{\text{calc}} = 1.49 < t_{\text{tab}} = 2.776$, $p = 0.95$, recovery 99.8%, RSD < 0.33%), demonstrating reliability for environmental monitoring.

In summary, the modified graphite paste electrode exhibits well-characterised electrochemical behaviour, adequate sensitivity for environmental Cu(II) monitoring, good selectivity toward common matrix ions, and validated accuracy relative to ICP-OES. The mechanistically transparent N,S-coordination approach provides a reproducible and cost-effective alternative to nanomaterial-based sensors, and represents a practical platform for trace-level heavy metal determination in environmental water samples.

Although several nanomaterial-based sensors reported in the literature achieve lower limits of detection, the present approach offers substantially simpler fabrication, reduced material cost, improved reproducibility, and elimination of environmentally hazardous mercury components, making it attractive for routine environmental monitoring applications.

5. Conclusions

A graphite paste electrode modified with 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione has been successfully developed for the electrochemical determination of Cu(II) ions in aqueous media. The incorporation of an N,S-donor ligand into a graphite–polystyrene matrix provides a simple, reproducible, and cost-effective electrode fabrication strategy without the need for complex nanomaterials.

Electrochemical characterization by cyclic voltammetry and impedance spectroscopy confirmed improved interfacial properties and predominantly diffusion-controlled mass transport, while scan-rate studies indicated quasi-reversible behavior of the Cu(II)/Cu(0) redox system. The enhanced analytical performance is attributed to coordination-driven preconcentration of Cu(II) ions at the electrode surface via N,S-bidentate binding.

Under optimized conditions, the developed sensor exhibited a linear response in the range of 0.01–0.4 $\mu\text{mol}\cdot\text{L}^{-1}$ with a limit of detection of 0.02 $\mu\text{mol}\cdot\text{L}^{-1}$. The method demonstrated good selectivity toward Cu(II) in the presence of common metal ions, while strong chelating agents significantly affected the response, supporting the proposed coordination mechanism.

The applicability of the method was validated through the analysis of Aydar–Arnasoy reservoir water samples; results were in good statistical agreement with ICP-OES ($t_{\text{calc}} = 1.49 < t_{\text{tab}} = 2.776$, $p = 0.95$), and spike–recovery experiments confirmed the absence of significant matrix effects (recovery 99.0–99.5%, RSD < 1.0%).

Overall, the proposed sensing strategy demonstrates that selective N,S-donor coordination chemistry can provide reliable trace-level Cu(II) determination without the need for nanomaterials or mercury-based electrodes. The combination of simple fabrication, satisfactory analytical performance, good selectivity, and successful validation against ICP-OES highlights the potential of this platform for routine environmental monitoring of copper contamination in natural waters.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/chemosensors14080172/s1>. Table S1. Cyclic voltammetry parameters of [Fe(CN)₆]^{4−}/[Fe(CN)₆]^{3−} redox couple at the unmodified and modified graphite paste electrodes at scan rates from 0.025 to 0.045 V·s^{−1}. Table S2. Fitted EIS parameters for the unmodified and modified graphite paste electrodes obtained using the Rs–(C || Rct) equivalent circuit. Figure

S1. Cyclic voltammograms of Cu(II) ions recorded at the modified graphite electrode in different buffer solutions: acetate buffer solution, phosphate buffer solution, and Britton–Robinson buffer solution. Figure S2. Cyclic voltammograms of Cu(II) ions recorded at the unmodified graphite electrode in the supporting electrolyte solution. Conditions: $C(\text{Cu}^{2+}) = 0.1 \mu\text{M}$; scan rate = $0.01\text{--}0.06 \text{ V}\cdot\text{s}^{-1}$. Figure S3. Cyclic voltammetric response of the modified graphite electrode in sulfuric acid media at different pH values without Cu(II) ions. The featureless voltammograms confirm that the observed current changes in subsequent measurements originate from Cu(II) ions rather than from the background electrolyte or the electrode modifier. Figure S4. DPV responses of the modified graphite electrode for (a) blank solution and (b) Cu(II) ions under identical experimental conditions.

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Conflicts of Interest: Author Nargiza Atakulova is employed by Almaliq Mining and Metallurgical Combine. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as potential conflicts of interest.

Abbreviations

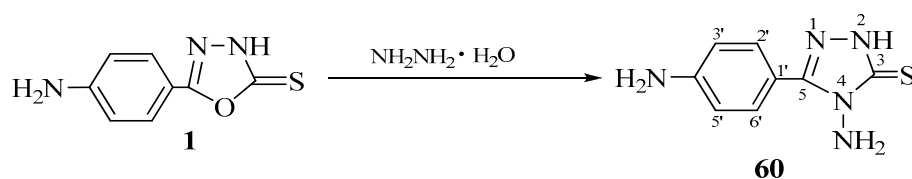
The following abbreviations are used in this manuscript:

Abbreviation	Full form
CV	Cyclic voltammetry
DPV	Differential pulse voltammetry
DPASV	Differential pulse anodic stripping voltammetry
ASV	Anodic stripping voltammetry
SWV	Square wave voltammetry
EIS	Electrochemical impedance spectroscopy
SEM	Scanning electron microscopy
FT-IR	Fourier-transform infrared spectroscopy
ICP-OES	Inductively coupled plasma optical emission spectrometry
GCE	Glassy carbon electrode
MGE	Modified graphite electrode
GPE	Graphite paste electrode
LOD	Limit of detection
LOQ	Limit of quantification
RSD	Relative standard deviation
WHO	World Health Organization
HSAB	Hard–Soft Acid–Base

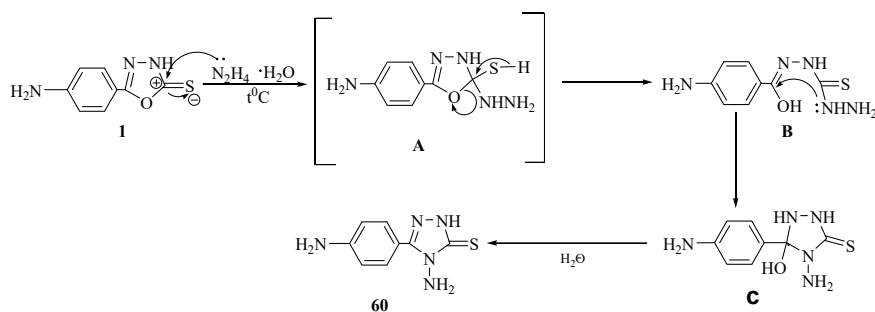
EDTA	Ethylenediaminetetraacetic acid
RGO	Reduced graphene oxide
PANI	Polyaniline
SWCNTs	Single-walled carbon nanotubes
OCP	Open-circuit potential
R _{ct}	Charge-transfer resistance
R _s	Solution resistance

Appendix A

For the synthesis of 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione, the first method was selected. The reaction was carried out by refluxing 5-(4-aminophenyl)-1,3,4-oxadiazole-2-thione in an excess of 80% hydrazine hydrate (NH₂NH₂·H₂O) for 8 h. Compound 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione was obtained as white crystals in 72% yield. Its IR spectrum showed absorption bands at 3268 cm⁻¹ (N–NH₂) and 3351 cm⁻¹ (NH₂–Ar), while in the ¹H NMR spectrum, compared with that of the initial 1,3,4-oxadiazole-2-thione 1, an additional singlet two-proton signal of the amino group attached to the N-4 nitrogen atom of the triazole ring was observed at 5.63 ppm. In addition, signals of the amino group on the aromatic ring appeared as a singlet at 5.71 ppm, and the four aromatic protons appeared as doublets at 6.62 ppm (2H, d, J = 8.7 Hz, H-3',5') and 7.73 ppm (2H, d, J = 8.6 Hz, H-2',6'). The signal of one NH proton attached to the N-2 nitrogen atom of the triazole ring appeared as a broad singlet at 13.31 ppm.



Its proposed synthesis mechanism:



At the first stage of the reaction, nucleophilic addition of a hydrazine molecule to the carbon atom of the thiocarbonyl group may occur, leading to the formation of 5-(4-aminophenyl)-2-hydrazinyl-2,3-dihydro-1,3,4-oxadiazole-2-thiol (A). Subsequently, cleavage of the C–O bond in the molecule takes place under the influence of nucleophilic groups (SH, NHNH₂), and opening of the oxadiazole ring results in the formation of 4-amino-N-(hydrazinecarbothioyl)benzohydrazonic acid (B). It should be emphasized that such thiohydrazides can very easily undergo heterocyclization with the formation of the intermediate 4-amino-5-(4-aminophenyl)-5-hydroxy-1,2,4-triazolidine-3-thione (C), which upon dehydration gives the expected product, 5-(4-aminophenyl)-4-amino-1,2,4-triazole-3(2H)-thione.

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