

Glutaraldehyde-Crosslinked Chitosan and Zinc Oxide Coating Reinforced with Polysulfone on Copper as a Platform for Electrochemical Formaldehyde Sensing

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Abstract: Formaldehyde monitoring requires electrochemical platforms with stable structures and reliable interfacial responses. This study aimed to prepare and characterize a Cu|CS–GLA/ZnO–PSf composite film on a copper substrate as a platform for further formaldehyde-sensing development. The film was characterized using FTIR, SEM–EDX, XRD, and cyclic voltammetry. FTIR supported the presence of features associated with chitosan, imine, polysulfone, and Zn–O, while SEM–EDX revealed a heterogeneous polymer-rich coating with Zn- and O-containing domains distributed non-uniformly. XRD indicated a predominantly amorphous or poorly crystalline structure. Cyclic voltammetry showed scan-rate-dependent peak separations, with ΔE_p increasing from 0.632 to 0.777 V in citrate buffer and from 0.320 to 0.560 V in the ferri/ferrocyanide system, indicating strongly non-ideal interfacial kinetics. Overall, the Cu|CS–GLA/ZnO–PSf interface provides a structurally and electrochemically characterized basis for further formaldehyde-sensing development.

Keywords: chitosan, cyclic voltammetry, formaldehyde sensing, polysulfone, zinc oxide

Abstrak: Pemantauan formaldehida memerlukan platform elektrokimia dengan struktur yang stabil dan respons antarmuka yang andal. Penelitian ini bertujuan untuk menyiapkan dan mengarakterisasi film komposit Cu|CS–GLA/ZnO–PSf pada substrat tembaga sebagai platform untuk pengembangan lebih lanjut sensor formaldehida. Film dikarakterisasi menggunakan FTIR, SEM–EDX, XRD, dan voltametri siklik. FTIR mendukung keberadaan fitur yang berkaitan dengan kitosan, imina, polisulfon, dan Zn–O, sedangkan SEM–EDX menunjukkan lapisan heterogen yang kaya polimer dengan domain yang mengandung Zn dan O yang terdistribusi secara tidak homogen. XRD menunjukkan struktur yang dominan amorf atau memiliki kristalinitas rendah. Voltametri siklik menunjukkan pemisahan puncak yang bergantung pada laju pindai, dengan ΔE_p meningkat dari 0,632 menjadi 0,777 V dalam buffer sitrat dan dari 0,320 menjadi 0,560 V dalam sistem feri/ferrosianida, yang menunjukkan kinetika antarmuka yang sangat tidak ideal. Secara keseluruhan, antarmuka Cu|CS–GLA/ZnO–PSf memberikan dasar yang telah dikarakterisasi secara struktural dan elektrokimia untuk pengembangan lebih lanjut sensor formaldehida.

Kata kunci: kitosan, polisulfon, sensor formaldehida, seng oksida, voltametri siklik

INTRODUCTION

Formaldehyde adulteration (“formalin”) in foods remains a serious safety concern because exposure is associated with adverse health effects and has been evaluated by authoritative bodies as carcinogenic to

humans, motivating routine monitoring beyond centralized laboratories (IARC 2006). Conventional confirmatory methods for formaldehyde determination, including high-performance liquid chromatography (HPLC) after derivatization, provide

high accuracy and selectivity (Wahed *et al.* 2016). However, these techniques are often less practical for rapid field screening due to instrument cost, time-consuming sample preparation/derivatization, and the need for skilled operators, which limits their applicability for routine food safety monitoring and on-site analysis (Bounegru & Bounegru 2023; Yang *et al.* 2024). Accordingly, electrochemical sensing platforms have gained attention because they offer the potential for portable, low-cost, and rapid measurements, while nanomaterial- and polymer-modified interfaces continue to be developed to improve analytical response and signal stability (Akitoye *et al.* 2024; Bard & Zoski 2015).

A key determinant of electrochemical sensor performance is the working-electrode interface, where electron-transfer kinetics, accessible active sites, and coating integrity collectively govern sensitivity, repeatability, and signal stability. Chitosan is widely adopted as a functional polymer matrix due to its biocompatibility, film-forming ability, and chemical tunability; however, chitosan coatings can be mechanically fragile and may present interfacial resistance that undermines durability and voltammetric reproducibility under repeated cycling (Bashal *et al.* 2022; Liu *et al.* 2020; Petrucci *et al.* 2021; Saisa *et al.* 2020). To address these limitations, metal-oxide nanoparticles, particularly ZnO, are often incorporated to provide additional electroactive interfacial sites and modify the electrochemical response. ZnO–chitosan matrices have also been reported to influence electrochemical behavior at sensing interfaces (Akitoye *et al.* 2024; Bounegru & Bounegru 2023; Eljali *et al.* 2017). Previous studies on Cu-supported crosslinked chitosan–glutaraldehyde/ZnO electrodes have demonstrated a structurally integrated interface with reproducible cyclic-voltammetric behavior, providing a basis for further electrochemical sensing development (Murniati *et al.* 2026).

Despite these advances, the mechanical robustness of thin polymer coatings remains an important consideration for practical and repeatable electrochemical measurements, particularly for drop-cast films on low-cost metallic substrates. Film cracking, delamination, and morphological heterogeneity may contribute to baseline drift and poor measurement-to-measurement consistency.

Here, we address this limitation through an integrated and mechanically reinforced coating strategy on copper, denoted Cu|CS–GLA/ZnO–PSf, building on previous work with related Cu/PS–CS–GA/ZnO composite electrodes (Afiyah *et al.* 2025; Murniati *et al.* 2024). In this architecture, (i) glutaraldehyde crosslinking is intended to stabilize the chitosan network through imine formation, (ii) ZnO provides additional inorganic interfacial sites, and (iii) polysulfone acts as a mechanically and chemically robust polymeric component.

Crosslinked chitosan networks are well established to form more stable polymer structures (Tamer *et al.* 2024), while polysulfone-based materials are recognized for their mechanical and chemical stability and can be modified with polymeric additives to tune structural properties (Das *et al.* 2019; Aprillianti *et al.* 2024). The novelty of this work lies in combining chemical stabilization, ZnO incorporation, and polysulfone reinforcement within a single thin-film architecture on copper, thereby establishing a structurally characterized platform for subsequent electrochemical formaldehyde-sensing studies.

MATERIALS AND METHODS

Materials and Instrumentation

Chitosan (degree of deacetylation $\approx 85\%$), zinc oxide (ZnO) nanopowder (<100 nm), and glutaraldehyde ($C_5H_8O_2$) solution (25 wt% in water) were purchased from Sigma-Aldrich and used as received. Polysulfone (PSf) was supplied by Solvay. Acetic acid (CH_3COOH), potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium chloride (KCl), citric acid ($C_6H_8O_7$), and sodium citrate ($Na_3C_6H_5O_7$) were of analytical grade. Deionized water was used throughout the experiments.

Electrochemical measurements were performed using a CHI660E electrochemical workstation (CH Instruments, USA) in a conventional three-electrode configuration, with the Cu|CS–GLA/ZnO–PSf film electrode as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and a platinum (Pt) wire as the counter electrode. Fourier-transform infrared (FTIR) spectra were recorded using a Shimadzu IRSpirit-T spectrophotometer over the range of $400\text{--}4000\text{ cm}^{-1}$. Surface morphology and elemental composition were examined using a JEOL JSM-6510LA scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (SEM–EDS). X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex 600 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$).

Preparation of CS–GLA/ZnO–PSf nanocomposite suspension

Chitosan (2% w/v) was dissolved in 1% (v/v) acetic acid (CH_3COOH) and magnetically stirred for 24 h at room temperature. Zinc oxide (ZnO, 0.6% w/v) was dispersed in 1% acetic acid and ultrasonicated for 30 min. Polysulfone (PSf, 5% w/v) was dissolved in *N,N*-dimethylformamide (DMF, C_5H_7NO) at $60\text{ }^\circ\text{C}$ for 4 h. The nanocomposite slurry was prepared by mixing the chitosan solution with the ZnO dispersion, followed by the addition of glutaraldehyde ($C_5H_8O_2$) to a final concentration of 1% (v/v). The PSf solution was then added, and the mixture was stirred for 2 h at room temperature to obtain a homogeneous suspension (Murniati *et al.* 2024).

Fabrication of Cu[CS–GLA/ZnO]–PSf composite film electrode

Copper (Cu) wire substrates (length 8 cm, diameter 0.15 cm) were mechanically polished, rinsed with deionized water, ultrasonicated sequentially in ethanol (C₂H₅OH) and water, and dried. A sensing zone with an effective length of 0.3 cm was defined using a capillary mask. The slurry (20 µL) was drop-cast onto the sensing zone and heat-treated at 60 °C for 30 min to form the Cu[CS–GLA/ZnO]–PSf thin film; electrodes were stored in a desiccator before testing.

The fabrication procedure of the Cu[CS–GLA/ZnO]–PSf composite film electrode is schematically illustrated in Figure 1.

Electrochemical measurements and data analysis

Cyclic voltammetry (CV) was conducted over a potential range of –1.0 to +1.0 V in 0.1 M citrate buffer (pH 4.0), prepared from citric acid (C₆H₈O₇) and sodium citrate (Na₃C₆H₅O₇), and in 0.01 M potassium ferricyanide (K₃[Fe(CN)₆]) containing 0.5 M potassium chloride (KCl). The scan rates were 25, 50, 75, and 100 mV s^{–1}. The anodic and cathodic peak currents (*I*_{pa} and *I*_{pc}) and peak potentials (*E*_{pa} and *E*_{pc}) were obtained from the voltammograms. The peak-to-peak separation was calculated as:

$$\Delta E_p = E_{pa} - E_{pc} \dots (1)$$

and the peak-current ratio was calculated as:

$$\left| \frac{I_{pa}}{I_{pc}} \right| \dots (2)$$

The formal potential was estimated as:

$$E^o = \frac{E_{pa} + E_{pc}}{2} \dots (3)$$

Scan-rate dependence was evaluated using the relationships *I*_p versus *v*, *I*_p versus *v*^{1/2}, and log *I*_p versus log *v*. Linear relationships were expressed as:

$$I_p = a + bv \dots (4)$$

and,

$$I_p = a + bv^{1/2} \dots (5)$$

while the log–log relationship was expressed as:

$$\log I_p = \log a + b \log v \dots (6)$$

where *I*_p is the peak current, *v* is the scan rate, *a* is the intercept or proportionality constant, and *b* is the slope; in the log–log relationship, *b* represents the kinetic exponent. Values of *b* approaching 0.5 indicate predominantly diffusion-controlled behavior, whereas values approaching 1.0 indicate predominantly surface-controlled behavior. Deviations from these limiting values were interpreted as mixed or non-ideal electrochemical behavior.

Linear regression and the coefficient of determination (*R*²) were used to evaluate the goodness of fit. All measurements were performed in triplicate, and regression analysis and plotting were carried out using OriginPro 2023 and Microsoft Excel 365 (Gunawan *et al.* 2025; Murniati *et al.* 2012a, 2012b).

RESULTS AND DISCUSSION

FTIR Analysis of Cu[CS–GLA/ZnO]–PSf Nanocomposite Film

The FTIR spectrum supports the presence of chitosan (CS), glutaraldehyde (GLA), zinc oxide (ZnO), and polysulfone (PSf) within the composite film (Figure 2). A broad absorption band centered at

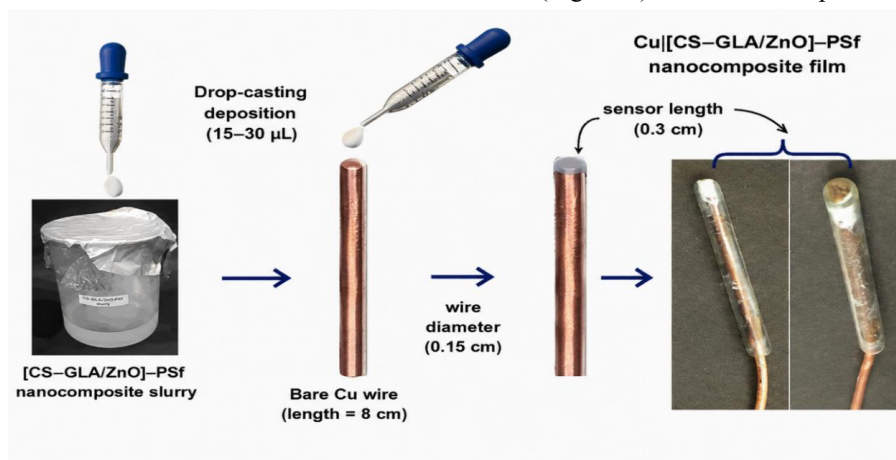


Figure 1. Schematic illustration of the fabrication of the Cu[CS–GLA/ZnO]–PSf nanocomposite film electrode by drop-casting. The CS–GLA/ZnO–PSf nanocomposite slurry was deposited onto a bare copper wire substrate (length = 8 cm, diameter = 0.15 cm), followed by drying to form a coated sensing region with an effective length of 0.3 cm.

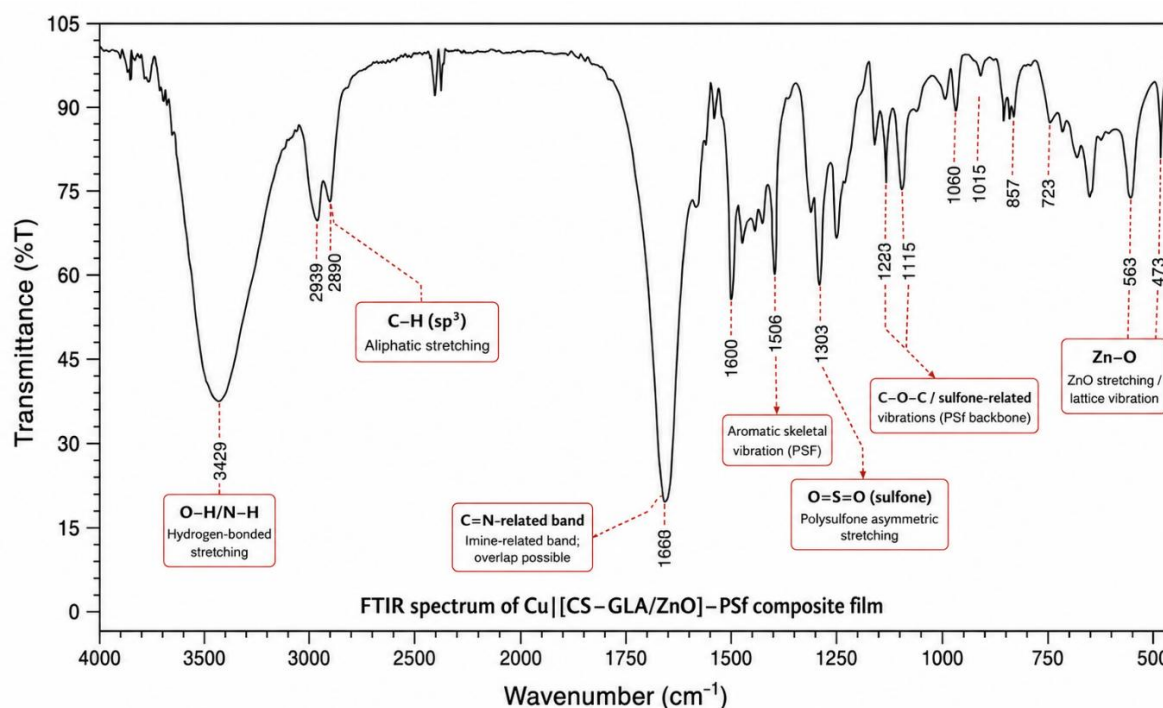


Figure 2. FTIR spectrum of the Cu|CS–GLA/ZnO–PSf composite film over the range of 400–4000 cm^{-1} , highlighting bands associated with chitosan (O–H/N–H and aliphatic C–H), an imine-related/overlapping band, polysulfone (aromatic skeletal, O=S=O, and backbone vibrations), and Zn–O lattice vibrations

approximately 3429 cm^{-1} is assigned to overlapping O–H and N–H stretching vibrations, characteristic of hydrogen-bonded hydroxyl and amine groups in the chitosan matrix (Silverstein *et al.* 2005). The bands at approximately 2939 and 2890 cm^{-1} are attributed to aliphatic C–H stretching vibrations, indicating that the chitosan backbone remains detectable after composite formation.

A strong band observed at approximately 1666 cm^{-1} may contain overlapping contributions from imine-related C=N stretching, residual amide vibrations of chitosan, and polymer skeletal vibrations. Therefore, this band is interpreted cautiously as an imine-related feature rather than as definitive evidence of Schiff-base formation. Nevertheless, its presence is consistent with the expected reaction between the aldehyde groups of GLA and the primary amine groups of chitosan. Similar imine-related bands have been reported for glutaraldehyde-crosslinked chitosan systems (Abd El Hady *et al.* 2021).

The presence of PSf is supported by the band at approximately 1506 cm^{-1} , associated with aromatic skeletal vibrations, together with a strong band at approximately 1303 cm^{-1} assigned to asymmetric O=S=O stretching. Additional bands at approximately 1223 and 1115 cm^{-1} are consistent with C–O–C and sulfone-related backbone vibrations of polysulfone-based materials (Dumbrava *et al.* 2025).

ZnO incorporation is supported by the low-wavenumber bands at approximately 563 and 473

cm^{-1} , which are assigned to Zn–O lattice vibrations. Overall, the simultaneous presence of chitosan-related, imine-related, sulfone, polysulfone-backbone, and Zn–O bands supports the formation of the CS–GLA/ZnO–PSf composite film. However, FTIR analysis alone does not establish the mechanical stability or electrochemical reproducibility of the electrode, which require complementary morphological and electrochemical characterization.

Morphology and elemental distribution of the Cu|CS–GLA/ZnO–PSf composite film (SEM–EDX)

SEM observations show a heterogeneous coated surface consisting of a continuous polymer-rich matrix with discrete brighter particles, clustered domains, and rosette-like or lamellar features at different magnifications (Figure 3). The persistence of these features across the examined areas indicates localized compositional heterogeneity within the cast composite film. However, the brighter structures should not be assigned exclusively to ZnO based on SEM contrast alone, because their chemical identity requires correlation with the corresponding elemental maps.

The polymeric matrix provides the structural framework for incorporation of the inorganic component, while localized particle-rich regions may contribute additional interfacial sites. In polysulfone-containing chitosan composites, polymer blending can also improve film integrity and reduce the

susceptibility of chitosan-rich coatings to cracking or delamination (Alawady *et al.* 2020). Nevertheless, mechanical reinforcement and adhesion cannot be established from SEM morphology alone and should therefore be interpreted as structural implications rather than directly measured properties.

The EDX spectrum confirms the presence of the principal elements expected from the composite coating (Figure 4). Carbon and oxygen are the dominant components, consistent with the organic polymer matrix, while sulfur provides a characteristic elemental marker for polysulfone. Zinc confirms

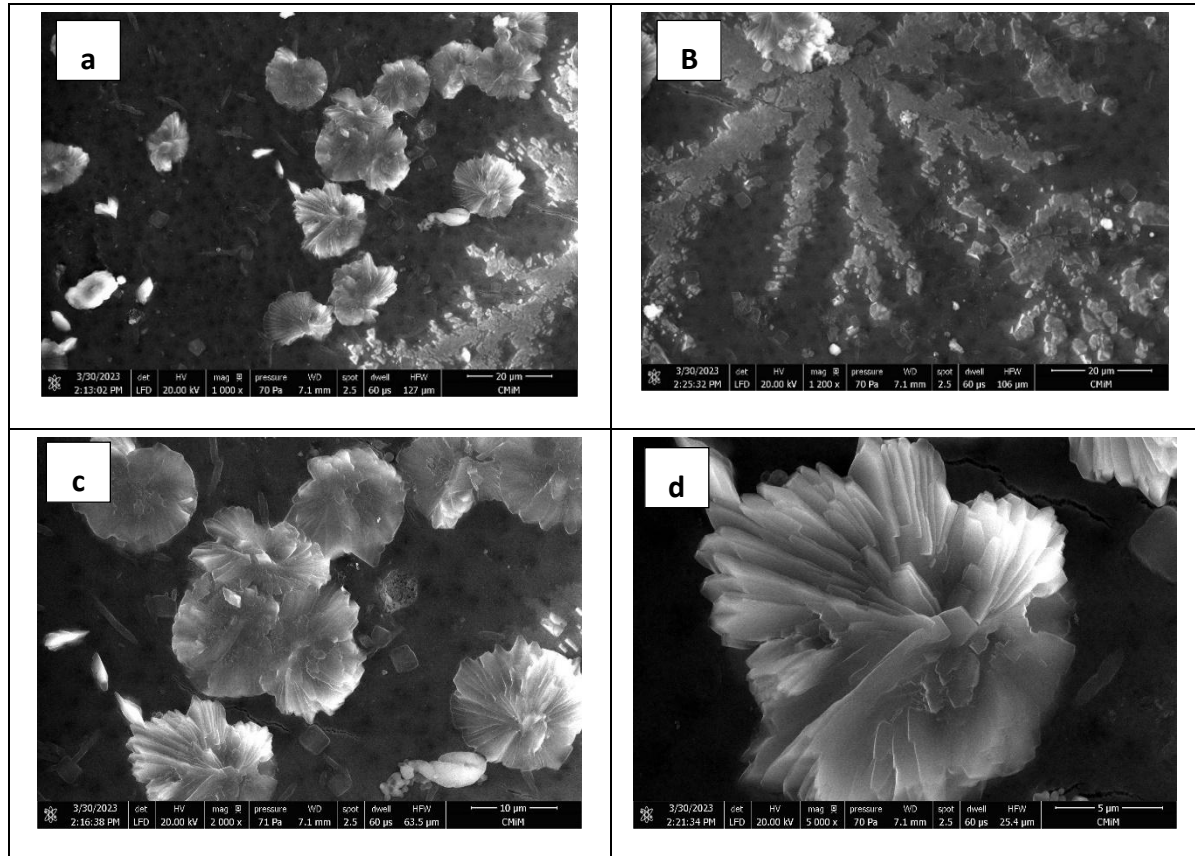


Figure 3. SEM micrographs of the Cu|CS–GLA/ZnO–PSf composite film at (a) 1,000× (scale bar: 20 µm), (b) 1,200× (20 µm), (c) 2,000× (10 µm), and (d) 5,000× (5 µm). The images show a heterogeneous film surface containing discrete bright particles, clustered domains, and rosette-like/lamellar features; their elemental composition is further evaluated by EDX analysis

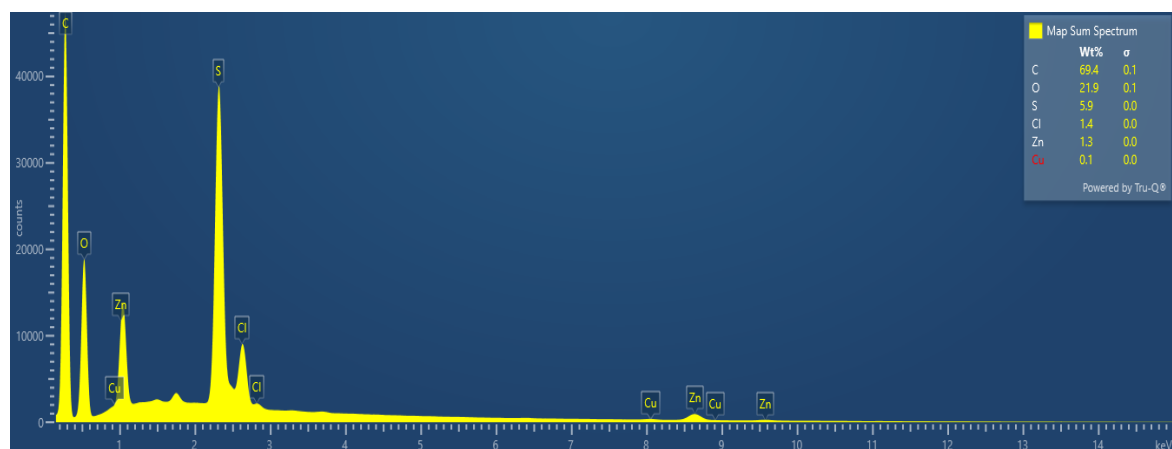


Figure 4. EDX spectrum of the Cu|CS–GLA/ZnO–PSf composite film showing C and O as the dominant matrix-associated elements, S as a polysulfone marker, Zn supporting ZnO incorporation, Cl as a residual element, and Cu originating predominantly from the underlying copper substrate

incorporation of the Zn-containing component, whereas the weak Cu signal originates primarily from the underlying copper substrate. A detectable Cl signal is also present and is attributed to residual chloride-containing species. These elemental fingerprints are consistent with SEM–EDX characterization of polymer/metal-oxide composite interfaces (Medany *et al.* 2024).

Elemental mapping provides additional information on the spatial distribution of the inorganic and polymer-associated components (Figures 5 and 6). Zn and O are distributed throughout the analyzed region with localized areas of higher intensity, supporting the presence of Zn-containing/O-containing domains within the polymer film. Their spatial distributions show partial correspondence rather than complete overlap, indicating a heterogeneous distribution of the inorganic component. In related ZnO–chitosan systems, such localized Zn-containing domains have been associated with increased interfacial interaction at electrode surfaces (Liu *et al.* 2020).

Importantly, the Cl map shows pronounced enrichment in several rosette-like features, indicating that the bright structures observed in the SEM images cannot be attributed solely to ZnO. Sulfur is comparatively broadly distributed, consistent with the presence of polysulfone throughout the coating, while carbon represents the organic matrix and Cu is associated predominantly with the underlying substrate. Overall, the SEM–EDX results demonstrate a chemically heterogeneous composite coating containing a continuous polymer-rich phase together with spatially localized Zn-, O-, and Cl-containing domains. This morphology provides a structurally plausible basis for the non-ideal interfacial electrochemical behavior observed in the cyclic-voltammetry analysis.

X-ray Diffraction (XRD): Phase signature of the Cu|CS–GLA/ZnO–PSf composite film

The XRD pattern of the Cu|CS–GLA/ZnO–PSf composite film is dominated by a broad diffuse halo rather than distinct sharp Bragg reflections, indicating that the analyzed coating is predominantly amorphous or poorly crystalline. In contrast, the zincite (ZnO) reference exhibits intense and narrow diffraction peaks characteristic of long-range crystalline order (Figure 7).

No clearly resolved ZnO reflections are observed in the composite-film pattern under the present measurement conditions. This may result from the relatively low inorganic fraction, dispersion of ZnO within the polymer-rich matrix, and/or reduced crystallinity of the embedded Zn-containing phase, all of which can decrease the intensity and broaden the diffraction features of the inorganic component (Alshammari 2022). Practically, the detectability of a minor crystalline phase by powder XRD can approach ~1 wt% depending on matrix/background and measurement conditions, and reported limits may fall below 1 wt% for favorable cases (Beköz Üllen 2022).

The XRD result should therefore be interpreted together with the complementary FTIR and SEM–EDS evidence. The Zn–O-related FTIR bands support the presence of Zn–O bonding, while EDX confirms the presence of Zn within the composite film. Taken together, these results indicate that the Cu|[CS–GLA/ZnO]–PSf coating is predominantly amorphous and contains Zn species in a dispersed and/or low-crystallinity form that is not readily resolved as a distinct crystalline ZnO phase by XRD (Murniati *et al.* 2024).

Scan-rate dependence and peak metrics of Cu|CS–GLA/ZnO–PSf in citrate buffer and ferri/ferrocyanide

Cyclic voltammetry (CV) of the Cu|CS–GLA/ZnO–PSf electrode was recorded at scan rates

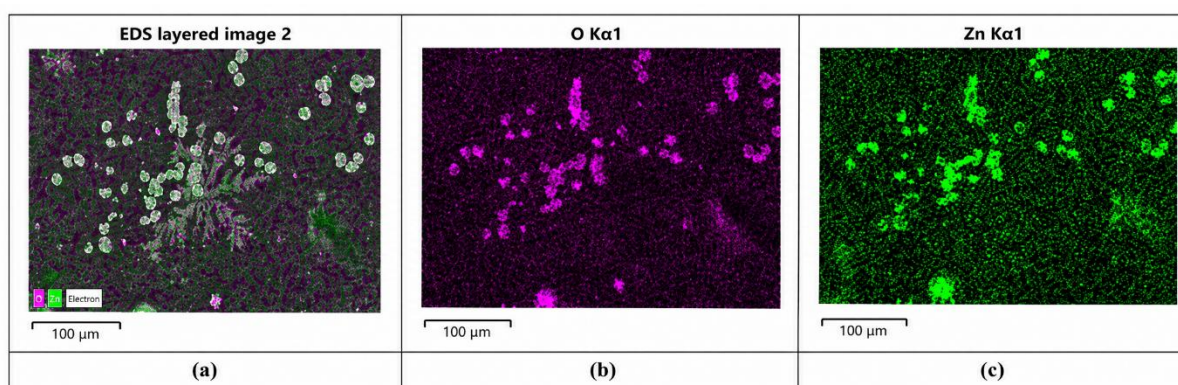


Figure 5. SEM–EDX overlay and elemental maps of the Cu|CS–GLA/ZnO–PSf composite film. (a) SEM–EDX overlay of the analyzed area showing a heterogeneous coated surface with discrete clustered features; (b) O Kα1 elemental map showing oxygen distributed throughout the analyzed region with localized O-enriched areas; and (c) Zn Kα1 elemental map showing Zn distributed across the film with localized regions of higher intensity

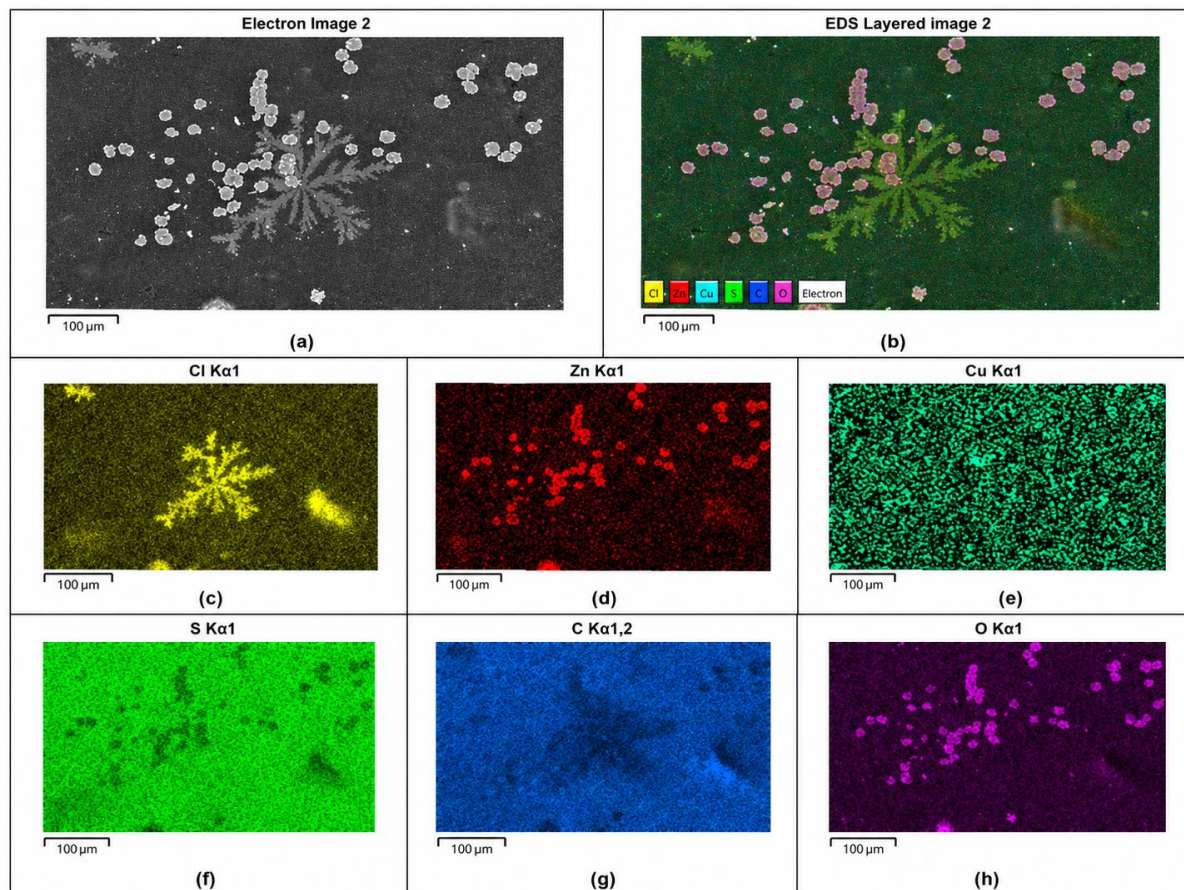


Figure 6. SEM-EDX characterization of the Cu|CS-GLA/ZnO-PSf composite film. (a) SEM electron image showing a heterogeneous coated surface with discrete bright particles, localized aggregates, and rosette-like features; (b) SEM-EDX overlay showing the spatial relationship between surface morphology and elemental signals; and (c–h) elemental maps of Cl, Zn, Cu, S, C, and O, respectively. The Cl map shows localized enrichment that partially corresponds to several rosette-like features, whereas Zn and O are distributed throughout the analyzed area with localized regions of higher intensity. Sulfur is broadly distributed and supports the presence of polysulfone, carbon represents the organic composite matrix, and Cu is attributed predominantly to the underlying copper substrate

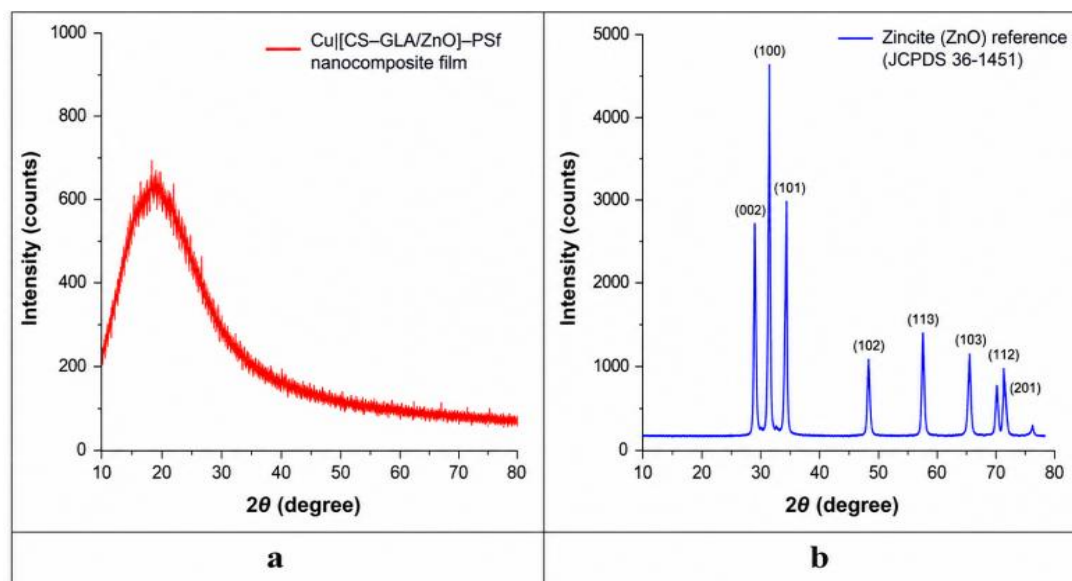


Figure 7. XRD patterns of (a) Cu|CS-GLA/ZnO-PSf composite film and (b) zincite (ZnO) reference

of 25–100 mV s^{-1} in 0.1 M citrate buffer (pH 4.0) and in 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]/0.5$ M KCl to evaluate the scan-rate-dependent behavior of the film-modified interface (Figure 8). In both electrolytes, the peak currents generally increased with increasing scan rate, consistent with the dependence of CV responses on mass transport and interfacial electron-transfer processes (Elgrishi *et al.* 2018; Wang 2001)

In citrate buffer, the cathodic peak current increased monotonically from -2.370 mA at 25 mV s^{-1} to -3.133 mA at 100 mV s^{-1} , while the anodic peak current increased from 2.879 to 3.257 mA. The peak-current ratio, $|I_{\text{pa}}/I_{\text{pc}}|$, progressively approached unity from 1.215 to 1.040 . However, ΔE_p increased from 0.632 to 0.777 V, accompanied by a negative shift in E_p' from -0.359 to -0.461 V. The large and scan-rate-dependent peak separation indicates pronounced electrochemical polarization and strongly non-ideal interfacial kinetics. Such behavior may arise when electron transfer is coupled with transport through a polymer-containing film and other interfacial resistive or capacitive contributions become increasingly significant at higher scan rates (Bard & Faulkner 2001).

For the ferri/ferrocyanide redox probe, I_{pc} increased from -5.249 mA at 25 mV s^{-1} to -5.716 mA at 75 mV s^{-1} and then remained nearly unchanged at -5.697 mA at 100 mV s^{-1} . The anodic current increased from 4.247 mA to approximately 5.08 mA over the same scan-rate range. Importantly, ΔE_p increased systematically from 0.320 to 0.560 V. These separations are substantially larger than expected for an ideal reversible one-electron redox process, demonstrating that the ferri/ferrocyanide response at the Cu|CS–GLA/ZnO–PSf interface is kinetically limited rather than ideally reversible. The slight current deviation observed at the highest scan rate may reflect increasing contributions from

interfacial polarization, capacitive current, and uncompensated resistance; however, these individual contributions cannot be quantitatively distinguished from CV data alone without complementary impedance measurements (Morales & Risch 2021).

To further examine the electrochemical kinetics, the anodic and cathodic peak currents were analyzed as functions of v and $v^{1/2}$, together with analysis of $\log I_p$ versus $\log v$. In citrate buffer, I_{pa} showed linear relationships with both v ($R^2 = 0.958$) and $v^{1/2}$ ($R^2 = 0.933$), whereas $|I_{\text{pc}}|$ exhibited even stronger correlations with v ($R^2 = 0.995$) and $v^{1/2}$ ($R^2 = 0.981$). For the ferri/ferrocyanide system, the anodic response showed weaker linearity with v ($R^2 = 0.636$) and $v^{1/2}$ ($R^2 = 0.720$), whereas the cathodic response correlated more strongly with $v^{1/2}$ ($R^2 = 0.901$) than with v ($R^2 = 0.839$). These results indicate that the scan-rate dependence cannot be described by a single ideal diffusion- or surface-controlled model (Figure 9).

The $\log I_p$ – $\log v$ analysis further indicated strongly non-ideal kinetic behavior of the Cu|CS–GLA/ZnO–PSf interface. The calculated b -values were 0.091 and 0.201 for the anodic and cathodic processes, respectively, in citrate buffer, and 0.127 and 0.064 for the corresponding ferri/ferrocyanide responses. These values are substantially lower than those expected for ideal diffusion-controlled ($b \approx 0.5$) or surface-controlled ($b \approx 1.0$) processes, indicating that the observed current response does not follow a single classical kinetic regime. The low b -values, together with the large and scan-rate-dependent ΔE_p , suggest that the electrochemical response is affected by significant interfacial kinetic limitations and by transport through the composite film rather than by unrestricted diffusion alone. Based on the practical criterion of obtaining the most stable and well-

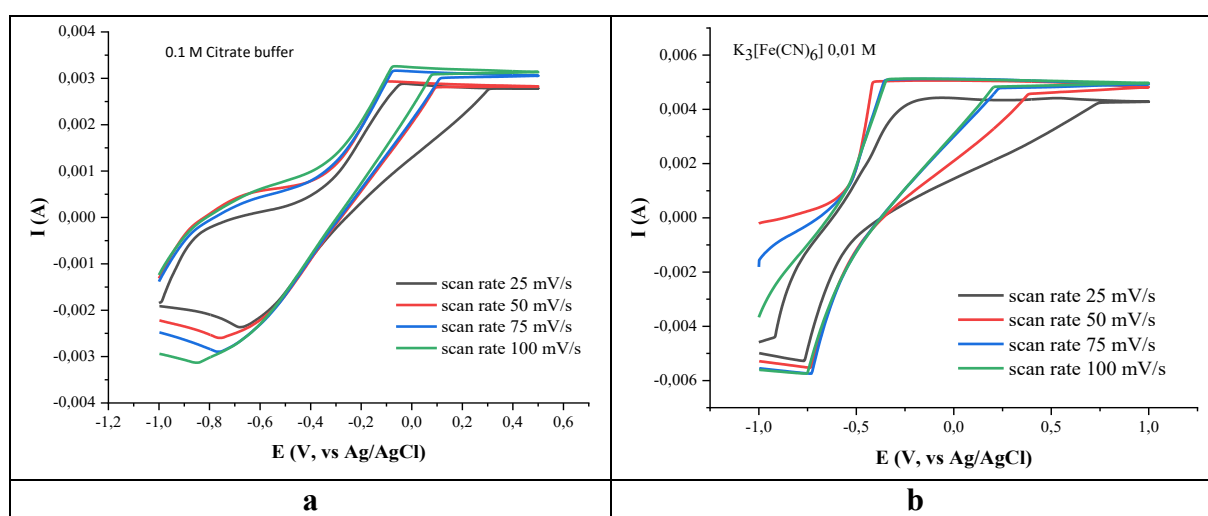


Figure 8. Scan-rate-dependent cyclic voltammograms of the Cu|CS–GLA/ZnO–PSf electrode. (a) CVs recorded in 0.1 M citrate buffer (pH 4.0) and (b) CVs recorded in 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]/0.5$ M KCl at scan rates of 25–100 mV s^{-1} .

defined cathodic response, 100 mV s^{-1} was selected for citrate buffer and 75 mV s^{-1} for ferri/ferrocyanide in KCl (Tables 1 and 2).

Although the I_p - $v^{1/2}$ relationship indicates that diffusion contributes to the overall response, the pronounced peak separation and its increase with scan rate show that the assumptions required for a

classical reversible Randles-Ševčík treatment are not fully satisfied. Therefore, the I_p - $v^{1/2}$ relationship was interpreted qualitatively as evidence of a diffusion-influenced contribution rather than being used to derive a quantitative electrochemically active surface area (EASA). Accordingly, the previously calculated EASA was not retained in the revised analysis

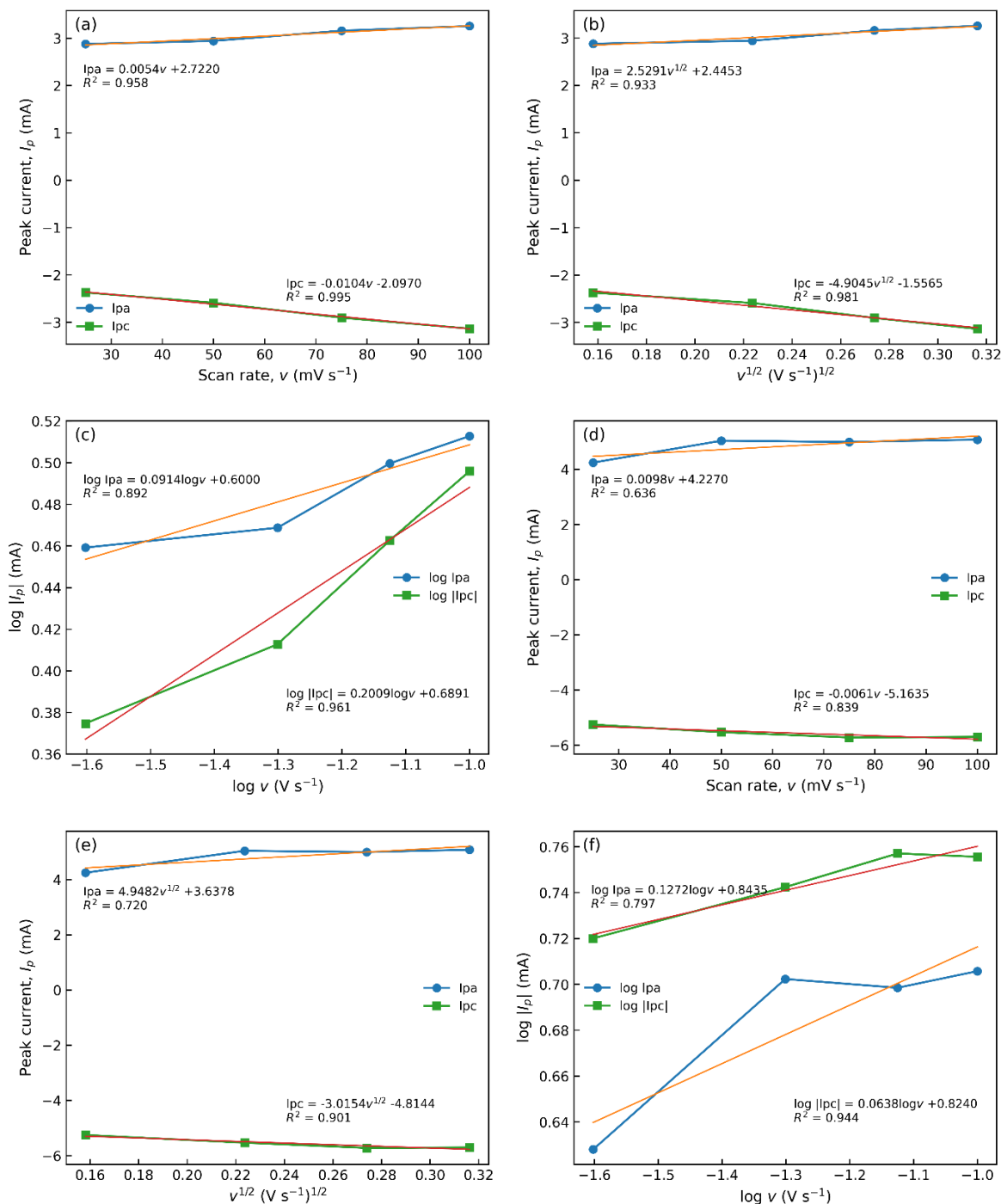


Figure 9. Scan-rate kinetic analysis of the Cu|CS–GLA/ZnO–PSf electrode: (a) I_p versus v in 0.1 M citrate buffer (pH 4.0), (b) I_p versus $v^{1/2}$ in citrate buffer, (c) $\log I_p$ versus $\log v$ in citrate buffer, (d) I_p versus v in 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]/0.5 \text{ M KCl}$, (e) I_p versus $v^{1/2}$ in 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]/0.5 \text{ M KCl}$, and (f) $\log I_p$ versus $\log v$ in 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]/0.5 \text{ M KCl}$

Table 1. CV peak potentials and currents of Cu|CS–GLA/ZnO–PSf in 0.1 M citrate buffer (pH 4.0) at different scan rates

Scan rate, v (mV s^{-1})	v (V s^{-1})	$v^{1/2}$ ($\text{V s}^{-1})^{1/2}$	E_{pa} (V)	E_{pc} (V)	ΔE_{p} (V)	$E^{\circ'}$ (V)	I_{pa} (mA)	I_{pc} (mA)	$ I_{\text{pa}}/I_{\text{pc}} $
25	0.025	0.158	−0.043	−0.675	0.632	−0.359	2.879	−2.370	1.215
50	0.050	0.224	−0.101	−0.757	0.656	−0.429	2.943	−2.587	1.138
75	0.075	0.274	−0.074	−0.763	0.689	−0.419	3.160	−2.902	1.089
100	0.100	0.316	−0.072	−0.849	0.777	−0.461	3.257	−3.133	1.040

$$E^{\circ'} = (E_{\text{pa}} + E_{\text{pc}})/2$$

Table 2. CV peak potentials and currents of Cu|CS–GLA/ZnO–PSf in 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ /0.5 M KCl at different scan rates

Scan rate, v (mV s^{-1})	v (V s^{-1})	$v^{1/2}$ ($\text{V s}^{-1})^{1/2}$	E_{pa} (V)	E_{pc} (V)	ΔE_{p} (V)	$E^{\circ'}$ (V)	I_{pa} (mA)	I_{pc} (mA)	$ I_{\text{pa}}/I_{\text{pc}} $
25	0.025	0.158	+0.310	−0.010	0.320	+0.150	4.247	−5.249	0.809
50	0.050	0.224	+0.335	−0.045	0.380	+0.145	5.039	−5.526	0.912
75	0.075	0.274	+0.355	−0.125	0.480	+0.115	4.995	−5.716	0.874
100	0.100	0.316	+0.370	−0.190	0.560	+0.090	5.079	−5.697	0.892

$$E^{\circ'} = (E_{\text{pa}} + E_{\text{pc}})/2$$

because its numerical value would not represent a rigorous electroactive-area determination under the present non-ideal kinetic conditions (Wang 2001).

CONCLUSION

A Cu|CS–GLA/ZnO–PSf composite film was prepared on a copper substrate and characterized in terms of its structural and electrochemical properties. FTIR supported the presence of chitosan-related functional groups, an imine-related crosslinking feature, polysulfone-associated vibrations, and Zn–O bonding. SEM–EDX confirmed a heterogeneous polymer-rich coating containing Zn-, O-, and S-associated components, while XRD indicated a predominantly amorphous or poorly crystalline structure with no clearly resolved ZnO reflections.

Electrochemical characterization showed large and scan-rate-dependent peak separations, with ΔE_{p} increasing from 0.632 to 0.777 V in citrate buffer and from 0.320 to 0.560 V in ferri/ferrocyanide. The corresponding b-values were 0.091 and 0.201 for the anodic and cathodic processes in citrate buffer and 0.127 and 0.064 for ferri/ferrocyanide, indicating strongly non-ideal interfacial kinetics. The $I_{\text{p}}-v^{1/2}$ relationship was therefore interpreted qualitatively rather than used for quantitative EASA determination. Practical scan rates of 100 mV s^{-1} in citrate buffer and 75 mV s^{-1} in ferri/ferrocyanide were selected. Overall, the Cu|CS–GLA/ZnO–PSf interface provides a structurally and electrochemically characterized platform for further formaldehyde-sensing development.

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