Development of Graphene-Polythiophene Modified Glassy Carbon Electrodes: A New Frontier in Electrochemical Ibuprofen Detection

[1]Iram Yasmin, [1]Muhammad Imran Kanjal*, [2]Uzma Sattar, [1]Muhammad Wasim Afzal, [3]Muhammad Irfan Ahamad, [4]Rana Muhammad Zulqarnain, [5]Lotfi Mouni**

[1]*Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Molecular Sciences, Henan University, Kaifeng, Henan 475004, China.*

[2] *Faculty of Chemistry, National & Local United Engineering Laboratory for Power Batteries, Northeast Normal University, Changchun 130024, China.*

[3]*College of Environmental and Resource Sciences, College of Carbon Neutral Modern Industry, Fujian Normal University, Fuzhou 350007, China.*

[4]*Department of Mathematics, Saveetha School of Engineering, SIMATS Thandalam, Chennai – 602105 Tamilnadu, India.*

[5]*Laboratory of Management and Valorization of Natural Resources and Quality Assurance, SNVST Faculty, University of Bouira 10000, Algeria.*

imrankanjal786@gmail.com*; mouni@univ-bouira.dz**

(Received on 25th August 2025, accepted in revised form 25th October 2025)

Summary: In this study, a novel electrochemical sensor for the determination of ibuprofen (IBU) is developed by modifying a glassy carbon electrode (GCE) with a composite of graphene (GR) and polythiophene (PTh). The unique combination of graphene's exceptional conductivity and surface area with the high electrochemical stability of polythiophene enhances the sensor's performance for IBU detection. The GR/PTh composite is synthesized via fluid/fluid interfacial polymerization and characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), providing essential insights into the morphology and structure of the composite material. The electrochemical behavior of IBU is investigated through differential pulse voltammetry (DPV) and cyclic voltammetry (CV), with a detection limit of 1.24 μM observed for IBU. The sensor demonstrates excellent reproducibility, stability, and selectivity, successfully distinguishing IBU from other common interferences. Moreover, the GR/PTh/GCE sensor exhibits a linear response for IBU concentrations ranging from 10 to 80 μM, making it a promising tool for the rapid and sensitive detection of IBU in pharmaceutical formulations and biological samples. This work highlights the potential of graphene-based nanocomposites for the development of advanced electrochemical sensors, offering a new approach to pharmaceutical analysis.

Keywords: Ibuprofen, Polythiophene, Graphene, Chemical oxidative-polymerization.

Introduction

In recent years, electrochemical sensors have experienced significant advancements, largely due to the integration of nanomaterials, which offer unique properties that traditional materials cannot provide [1, 2]. Graphene (GR), a two-dimensional carbon nanomaterial, has attracted considerable attention for its exceptional electrical conductivity, large surface area, mechanical strength, and chemical stability [3-5]. These unique properties make graphene an ideal candidate for various applications, including energy storage, catalysis, and sensing technologies [6-8]. However, its practical use in electrochemical sensors is often limited by challenges such as poor solubility, agglomeration tendencies, and limited electrochemical reactivity due to a lack of functional groups on its surface [9, 10]. To overcome these limitations, combining graphene with conducting polymers like polythiophene (PTh) has emerged as a promising strategy [3, 11, 12]. Polythiophene, a conjugated polymer known for its electrochemical stability and ease of synthesis, enhances the electrochemical properties of graphene by facilitating electron transfer [13-15]. This synergistic combination improves the overall performance of electrochemical sensors in terms of sensitivity, selectivity, and stability [16, 17]. Graphene-polythiophene composites have been shown to significantly boost the electrochemical behavior of electrodes, leading to superior sensor performance [12, 18]. Ibuprofen (IBU), a widely used non-steroidal anti-inflammatory drug (NSAID), presents detection challenges in complex samples like pharmaceutical formulations and biological matrices, primarily due to interference from other substances [19, 20]. Effective detection methods must provide high sensitivity and selectivity for accurate monitoring of IBU concentrations [5, 21-24]. In this study, a novel electrochemical sensor for the determination of ibuprofen (IBU) is developed by modifying a glassy

carbon electrode (GCE) with a composite of graphene (GR) and polythiophene (PTh). The unique combination of graphene's exceptional conductivity and large surface area with the high electrochemical stability of polythiophene enhances the sensor's performance for IBU detection. The electroactive surface area (ECSA) is a crucial factor influencing the sensitivity of electrochemical sensors, as it determines the available surface for analyte interaction. In this work, we quantitatively estimate the ECSA for bare GR, PTh, and the GR/PTh composite, and compare these values with those reported for other existing catalysts used in electrochemical ibuprofen detection.

Experimental

Chemicals

The thiophene monomer (99%), potassium dichromate (99.4%), acetic acid, graphite powder, hydrazine monohydrate (≥99%), potassium permanganate, hydrogen peroxide, and ibuprofen were sourced from Avanti's chemical supply, Merck, and Sigma Aldrich. Phosphate buffer solutions (PBS, 0.1 M) at various pH values (7.1) were prepared by mixing 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4 stock solutions. All other reagents, including hydrochloric acid, nitric acid, sulfuric acid, sodium nitrate, potassium nitrate, deionized water, and ethanol, were of analytical grade. Graphene (GR) was synthesized using hydrazine reduction.

Experimental design

For the electrochemical experiments, all voltammetry measurements were performed using a three-electrode setup, with the instruments connected to a PC. The three-electrode system included a glassy carbon electrode (GCE, 3.0 mm diameter, Sigma Aldrich), GR/PTh/GCE, GR/GCE, and PTh/GCE as the working electrodes. A platinum wire (1.0 mm in diameter) served as the counter electrode, while a silver-silver chloride electrode (3M NaCl) was used as the reference electrode. Differential pulse voltammetry, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry were conducted using a CHI730D electrochemical workstation (CH Instruments, Chenhua, China, Shanghai). All measurements were performed in triplicate, and data were processed using Origin Pro 8 software (Origin Lab, Northampton, USA).

Synthesis of Graphene (GR)

Graphene oxide was synthesized as a precursor for the preparation of graphene using a modified Hummers' method [25]. In this process, 5 g of sodium nitrate ($NaNO_3$), 15 g of graphite, and 180 ml of concentrated sulfuric acid (H_2SO_4) were mixed and stirred at 0 °C in a 2000 ml reaction flask placed in an ice bath. Then, 35 g of potassium permanganate ($KMnO_4$) was gradually added to the mixture while maintaining a controlled temperature of 35°C. The mixture was stirred for 2 hours. After a 30-minute resting period, the temperature was increased to 98 °C, and 460 ml of deionized water was slowly added to the suspension over 40 minutes.

Preparation of GR/PTh

The GR/PTh nanocomposite was prepared using the method given in [26]. A 0.3 g of purified thiophene (3.2 mmol/L) was dissolved in 10 mL of 1 M hydrochloric acid (HCl) solution. Under continuous vigorous stirring at room temperature, 0.18 g of potassium dichromate (0.8 mmol/L) was rapidly added to the thiophene solution. After about 5 minutes, the characteristic light brown color of polythiophene appeared, indicating the polymerization of thiophene. Polythiophene undergoes oxidative polymerization, resulting in a conducting polymer, but does not form an 'emeraldine salt' as seen in polyaniline. The solution was allowed to mix at room temperature for 3 hours. To purify the resulting polythiophene, the mixture was first washed with ethanol to remove unreacted monomers and other impurities. After washing, the product was vacuum dried at 60°C for 12 hours to ensure the removal of solvent traces, yielding a purified GR/PTh composite.

Preparation of GR/PTh/GCE

To prepare the modified electrode, the glassy carbon electrode (GCE) was first cleaned with 0.05 μm alumina powder and then ultrasonicated in Milli-Q water and acetone $(CH_3)_2CO$ for 5 minutes. The prepared GR/PTh nanocomposite was applied to the GCE (3 mm diameter), and the electrode surface was allowed to dry in air, leaving the GCE surface intact. The cyclic voltametric behavior of the electrode was tested in a 0.1 mM $K_3[Fe(CN)_6]$ solution with 0.1 M KCl as the electrolyte, at a scan rate of 100 mV/s, with the peak potential range set between 0 and 0.6 V. When the peak potential difference was approximately 92 mV, the electrode was deemed suitable for use, acknowledging that this value is slightly higher than the ideal 59 mV for a fully reversible one-electron system. This suggests some quasi-reversibility or resistance effects, but the electrode still demonstrated acceptable electrochemical performance under the experimental conditions.

Electroactive Surface Area (ECSA) Measurement

The electroactive surface area (ECSA) of the bare graphene (GR), polythiophene (PTh), and the GR/PTh composite was estimated using cyclic voltammetry (CV) at various scan rates. The Randles-Sevcik equation was used to calculate the ECSA, based on the relationship between the peak current (I_peak) and the scan rate (v). The ECSA was determined using the following equation:

$$I_{\text{peak}} = (2.69 \times 10^5) \times n \times A \times D^{1/2} \times v^{1/2} \times C$$

Where I_{peak} is the peak current, n is the number of electrons involved in the redox reaction, A is the electroactive surface area, D is the diffusion coefficient, v is the scan rate, and C is the concentration of the electroactive species. The linear relationship between peak current and the square root of the scan rate was used to estimate the ECSA for the GR/GCE, PTh/GCE, and GR/PTh/GCE electrodes.

Results and Discussion

Characterization

The SEM and TEM images provide essential insights into the morphology and structural characteristics of the materials used in this study, which are crucial for the development of the electrochemical sensor. The SEM image of graphene (GR) (Fig 1a) reveals a porous structure with a large surface area, showing irregular, wrinkled graphene nanosheets with varying degrees of overlap, which are beneficial for creating high-performance sensors by increasing the active surface area for analyte interaction and improving electron transport during electrochemical reactions. The TEM image (Fig 1b) confirms this with a detailed view of thin, elongated graphene sheets, showing well-defined edges and a stacked structure that enables high conductivity and efficient electron transfer. This is essential for the sensor's performance, as graphene's excellent conductivity allows for fast electron transfer rates and high sensitivity in detecting ibuprofen (IBU). The SEM image of the GR/PTh nanocomposite (Fig 1c) shows a uniform distribution of the materials, which may contribute to enhanced conductivity and improved stability, factors that support its long-term performance. The TEM image of the GR/PTh composite modified glassy carbon electrode (GCE) (Fig 1d) shows a well-adhered layer of the nanocomposite, indicating the successful integration of GR/PTh with the electrode to provide a stable and conductive surface for detecting IBU. The uniform coating ensures the sensor's reproducibility and stable performance, which is essential for real-time detection [27]. The innovative combination of graphene and polythiophene enhances the electrochemical properties of the GCE by synergistically complementing the high surface area, conductivity, and mechanical strength of graphene with the conductive polymer PTh, resulting in improved sensor performance, durability, and reproducibility [28].

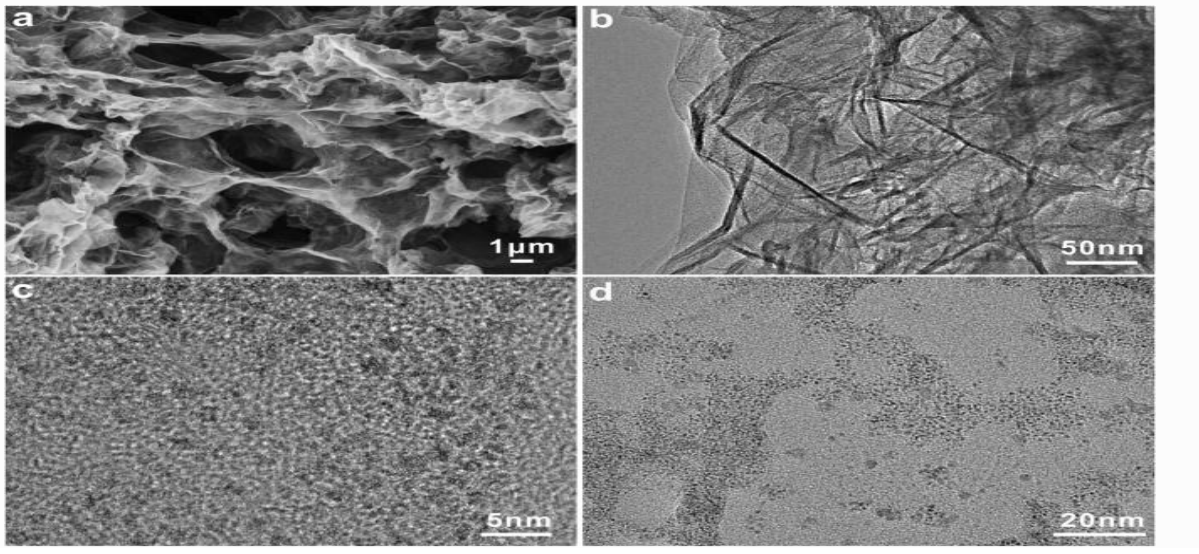

Fig 1**:** (a) SEM image of graphene (GR), (b) TEM image of graphene (GR), (c) SEM image of GR/PTh composite, and (d) TEM image of GR/PTh composite modified GCE.

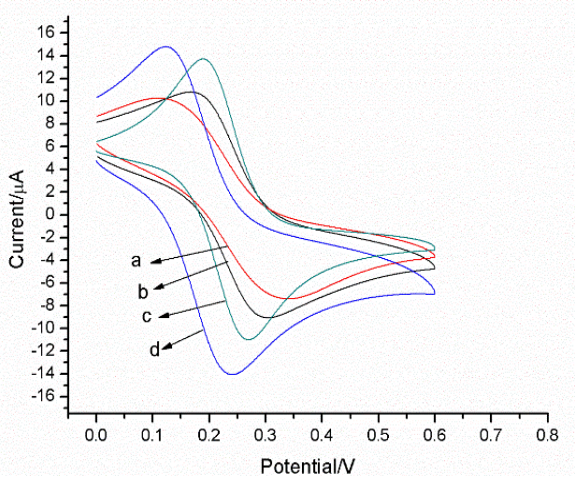

Fig 2: Cyclic voltammograms of unmodified GCE (a), PTh-modified GCE (b), GR-modified GCE (c), and GR/PTh/GCE (d) in 1 mM $K_3[Fe_2(CN)_6]$ solution with 0.1 M KCl, showing improved electrochemical performance at the GR/PTh/GCE electrode with smaller peak-to-peak separation and higher anodic peak current.

Electrochemical characterization

The electrochemical characterization of the modified electrodes, as shown in Fig 2, demonstrates the enhanced performance of the GR/PTh/GCE electrode compared to other modified electrodes. The cyclic voltammograms (CVs) for the unmodified GCE (a), PTh-modified GCE (b), GR-modified GCE (c), and GR/PTh/GCE (d) in a 1 mM $K_3[Fe_2(CN)_6]$ solution are displayed. The results show the presence of well-defined redox peaks, indicating that the modification of GCE with graphene and polythiophene significantly improves its electrochemical properties. The GR/PTh/GCE electrode exhibits the smallest peak-to-peak separation (ΔEp = 214 mV) compared to the GR/GCE (ΔEp = 295 mV), PTh/GCE (ΔEp = 336 mV), and bare GCE (ΔEp = 384 mV). This smaller ΔEp reflects the faster electron transfer rate at the GR/PTh/GCE, which is attributed to the enhanced electrical conductivity of the graphene component in the composite [29]. Additionally, the anodic peak current of GR/PTh/GCE (36.4 μA) is 1.23-fold, 1.26-fold, and 1.78-fold higher than that of the GR/GCE (29.6 μA), PTh/GCE (28.8 μA), and bare GCE (20.4 μA), respectively. This increase in current is due to the increased surface area and improved electrochemical activity of the composite material, especially the synergistic effects of graphene's large surface area and polythiophene's electrochemical properties [30]. The presence of three distinct redox peaks further supports the formation of a stable GR/PTh composite on the electrode surface, which facilitates enhanced electron transfer. The graphene is partially reduced at 0.25 V on the PTh-modified GCE, while the reduction occurs at 0.35 V on the bare GCE, suggesting that PTh enhances the interaction between graphene and the electrode surface. These results highlight the potential of the GR/PTh/GCE as a highly effective electrode for electrochemical applications, offering faster electron transfer and improved sensitivity, which is crucial for detecting ibuprofen and other electroactive compounds [31].

Cyclic Voltametric Behaviors of IBU at GR/PTh/GCE

In Fig 3, the electrochemical behavior of ibuprofen (IBU) was analyzed using cyclic voltammetry (CV) on various electrode modifications. Panel (a) shows the electrochemical response of ibuprofen at a bare glassy carbon electrode (GCE), which reveals weak redox peaks. The peak-to-peak separation (ΔEp) is 62 mV, with cathodic and anodic peak potentials (Epc = 0.310 V and Epa = 0.372 V, respectively), indicating a slow electron transfer process. In panel (b), the PTh-modified GCE demonstrates improved electrochemical behavior towards ibuprofen, with a reduced peak-to-peak separation (ΔEp = 48 mV) and shifted peak potentials (Epc = 0.358 V, Epa = 0.406 V), indicating better electron transfer. The GR-modified GCE (panel c) shows a capacitive current initially, but after adding 1×10^{-5} M IBU, well-defined redox peaks emerge at Epc = 0.350 V and Epa = 0.376 V, with a significantly smaller ΔEp of 26 mV. This small separation reflects faster electron transfer at the graphene-modified electrode. The GR/PTh/GCE (panel d) shows a remarkable enhancement in the anodic peak current (36.4 μA), which is 1.23-fold, 1.26-fold, and 1.78-fold higher than the currents observed for GR/GCE, PTh/GCE, and bare GCE, respectively. This increase is attributed to the larger surface area and enhanced electrocatalytic activity provided by the graphene-polythiophene composite [32]. The faster electron transfer and improved peak currents at GR/PTh/GCE highlight the synergistic effects of graphene and polythiophene in enhancing the electrode's electrochemical performance, making it highly suitable for sensitive and rapid detection of ibuprofen. [33] The results underscore the significant role of graphene in facilitating electron mobility, which is key for achieving high sensitivity in electrochemical sensors.

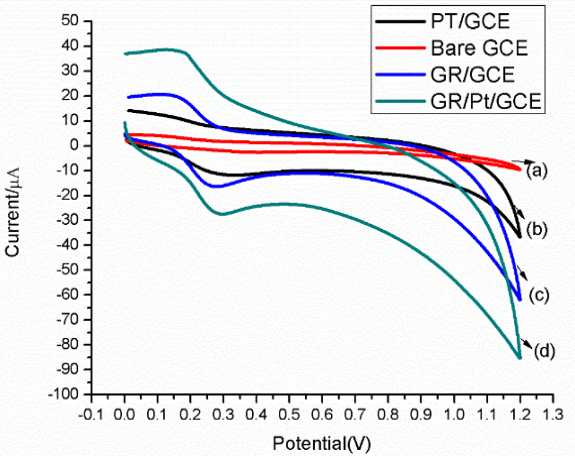

Fig 3**:** Cyclic voltammograms of the GR/PTh/GCE electrode in 0.5 mM ibuprofen solution at various electrode modifications: (a) bare GCE, (b) PTh-modified GCE, (c) GR-modified GCE, and (d) GR/PTh/GCE, showing enhanced electrochemical response at the GR/PTh/GCE.

Effect of Scan Rate

In Fig 4, the effect of scan rate on the cyclic voltammograms (CVs) of ibuprofen at the GR/PTh/GCE electrode in PBS (pH 7.1) is explored. Fig 4 (A) shows the CV curves of 10 μM ibuprofen at various scan rates (30–100 mV/s). As the scan rate increases, the anodic peak currents of ibuprofen also increase, which indicates that the scan rate influences the redox behavior of ibuprofen. The linear relationship between the peak current (I-P) and the square root of the scan rate further supports the notion that the electrochemical reaction of ibuprofen at the GR/PTh/GCE is diffusion-controlled. The regression equation, ipa = 56.421v^0.271 (where v is the scan rate in V/s), with a correlation coefficient of r = 0.994, shows a slope of approximately 0.27. This suggests that the electrochemical reaction of ibuprofen at the GR/PTh/GCE electrode is diffusion-controlled, as confirmed by the close relationship between the peak current (I_p) and the square root of the scan rate (v^1/2). Typically, a slope of around 1 is observed for processes that are adsorption-controlled, which would indicate a different mechanism at the electrode surface. The value of 0.27 aligns more with diffusion, which is typical for electrochemical reactions occurring at the modified glassy carbon electrode (GCE) surface under the experimental conditions. This is likely due to the high conductivity and electrochemical stability of the GR/PTh composite, which enhances the electron transfer and allows for efficient diffusion of ibuprofen molecules [34]. Fig 4(B) further complements this analysis by presenting a plot of Ip versus scan rate (v). This plot shows a clear linear relationship between the peak current and the scan rate, further confirming that the electrochemical reaction is primarily controlled by adsorption at the GR/PTh/GCE electrode. This behavior indicates that the adsorption of ibuprofen on the electrode surface contributes significantly to the redox process, which is enhanced by the unique π–π interactions between the ibuprofen and graphene, a feature attributed to the graphene component of the composite [35]. These results collectively demonstrate that the GR/PTh/GCE electrode offers a highly sensitive platform for detecting ibuprofen due to its enhanced electrochemical properties, fast electron transfer, and strong adsorption capacity.

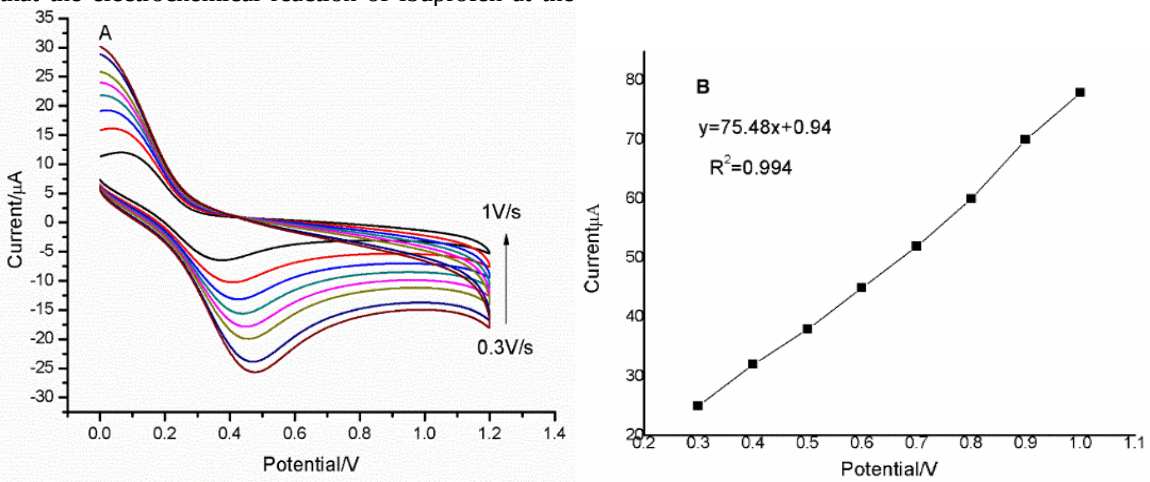

Fig 4: (A) Cyclic voltammograms of the GR/PTh/GCE electrode in the presence of 10 μM ibuprofen at varying scan rates (30–100 mV/s), demonstrating the adsorption-controlled electrochemical behavior; (B) Plot of peak current (Ip) versus scan rate (v).

The Effect of pH Values

The effect of pH on the electrochemical behavior of ibuprofen at the GR/PTh/GCE electrode is shown in Fig 5. As pH increases, the oxidation peak current reaches a maximum at pH 7.1, indicating the most favorable electrochemical conditions for ibuprofen oxidation. While the plot of the oxidation peak current versus pH (Fig 5B) does not demonstrate perfect linearity, the observed trend provides meaningful insights into the optimal pH for ibuprofen detection. The non-linearity is likely due to the complexity of the electrochemical oxidation process of ibuprofen, which may involve pH-dependent reaction mechanisms and interactions between ibuprofen and the electrode surface. This behavior is consistent with other electrochemical systems, where various factors contribute to the electrochemical response at different pH values [36, 37]. These results highlight the importance of pH optimization for enhancing the sensitivity and performance of the electrochemical sensor. The findings also underscore the robustness of the GR/PTh/GCE electrode, which can operate effectively across a range of pH values, but with the highest efficiency at neutral pH, making it suitable for practical applications in pharmaceutical analysis and environmental monitoring.

Calibration Plot

In Fig 6, the calibration plot for ibuprofen (IBU) detection using the GR/PTh/GCE electrode is shown. Differential pulse voltammetry (DPV) was employed to evaluate the sensor's response at different ibuprofen concentrations ranging from 10 to 80 μM. The results demonstrated a linear relationship between the anodic peak current and ibuprofen concentration, confirming that the GR/PTh/GCE electrode provides a wide and reliable detection range for ibuprofen, as shown in Fig 6A. To determine the sensitivity of the sensor, the limit of detection (LOD) and the limit of quantification (LOQ) were calculated. The LOD was determined using the signal-to-noise ratio (SNR), based on the following formula:

$$\mathrm{LOD} = \frac{3 \times \text{Standard deviation of the blank}}{\text{Slope of the calibration curve}}$$

The calculated LOD for ibuprofen was found to be 1.24 μM. This value represents the lowest concentration at which a significant electrochemical signal could be reliably detected, based on our experimental conditions. The LOQ was determined by establishing a signal-to-noise ratio of 10:1, which is commonly used to ensure accurate and reproducible measurements. The LOQ for ibuprofen was calculated to be approximately 1.25 μM, which is consistent with the LOD value and ensures that concentrations below this threshold may not provide reliable quantitative data. It is important to note that the calibration curve begins at 10 μM to ensure that the concentrations in the linear range are above the LOQ, ensuring accurate and reliable quantification. Therefore, the calibration range (10–80 μM) was chosen to avoid potential inaccuracies below the LOQ, where the sensor's performance may not be optimal [38, 39]. In Fig 7B, the current-time (I-t) curve of the GR/PTh/GCE electrode during ibuprofen oxidation is shown, which highlights the influence of aggregation time on the sensor's performance. As the oxidation time increases, the oxidation current increases, suggesting that the sensor's response is enhanced with longer accumulation periods. The peak current response reached its maximum at 20 seconds, after which no further significant increase in the current was observed. This behavior indicates that the oxidation reaction reaches completion within 20 seconds, and any further increase in accumulation time would not significantly affect the sensor's performance [40, 41]. The data in Fig 7B provide additional insight into the sensor's efficiency and stability by demonstrating that the sensor achieves near-complete oxidation of ibuprofen after 20 seconds. This optimized accumulation time ensures a substantial peak current, which enhances the sensitivity of the electrochemical sensor.

t curve measurement

In Fig 7, the performance of the GR/PTh/GCE electrode in detecting ibuprofen is evaluated by measuring the current-time (I-t) curve. The Fig shows the relationship between the oxidation current and the time of ibuprofen oxidation. The oxidation potential was fixed at 1.2 V, and the oxidation time was varied from 0 to 20 seconds. Initially, the current decays significantly as the oxidation period begins. After approximately 20 seconds, the current stabilization occurs, indicating that the oxidation reactions of ibuprofen are nearly complete by this time. As the aggregation time increases from 0 to 10 seconds, the recovery percentage improves from 23.0% to 95.2%. When the time reaches 20 seconds, the recovery percentage levels off, and further increases in aggregation time do not significantly enhance the recovery or oxidation reaction. The results suggest that a 20-second oxidation period is optimal for maximizing the sensor's response. This behavior indicates that the sensor achieves near-complete oxidation of ibuprofen within this time frame, and further increases in the collection time do not lead to substantial gains in current response [42, 43]. This experiment highlights

the importance of optimizing the aggregation time for effective ibuprofen detection, with the GR/PTh/GCE electrode showing excellent sensitivity and fast response times. The peak current response at 20 seconds is about three times larger than without aggregation, demonstrating the substantial effect of aggregation on enhancing the sensor's electrochemical performance [44]. These findings suggest that the GR/PTh/GCE electrode is highly efficient for rapid and sensitive ibuprofen detection in practical applications.

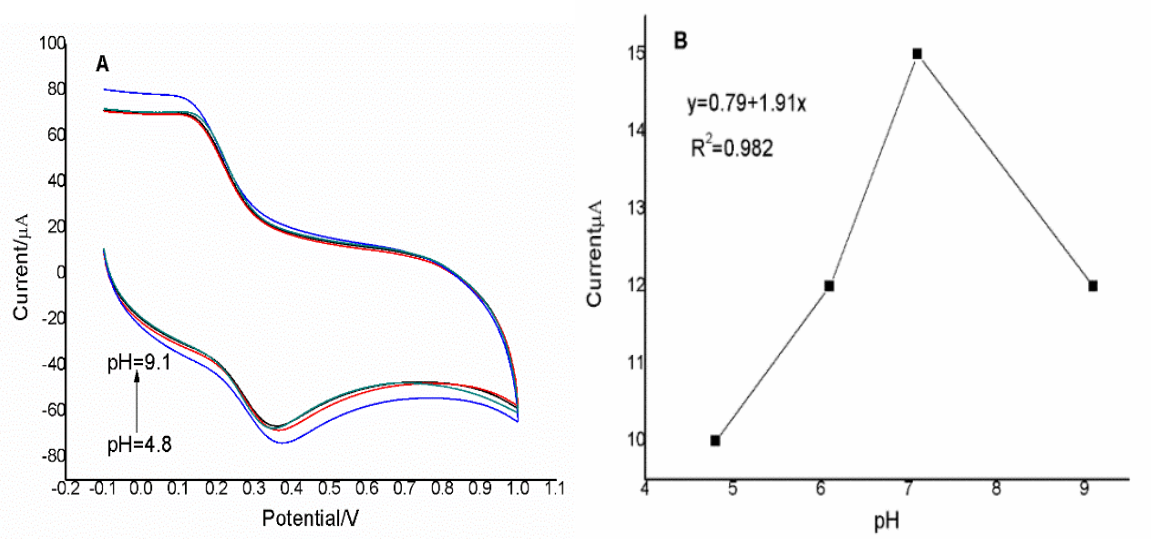

Fig. 5: Cyclic voltammograms of the GR/PTh/GCE electrode for 5 μM ibuprofen in PBS at different pH values (A). The plot of oxidation peak current versus pH (B) shows a trend, with non-linearity attributed to the complex electrochemical process and pH-dependent behavior of ibuprofen.

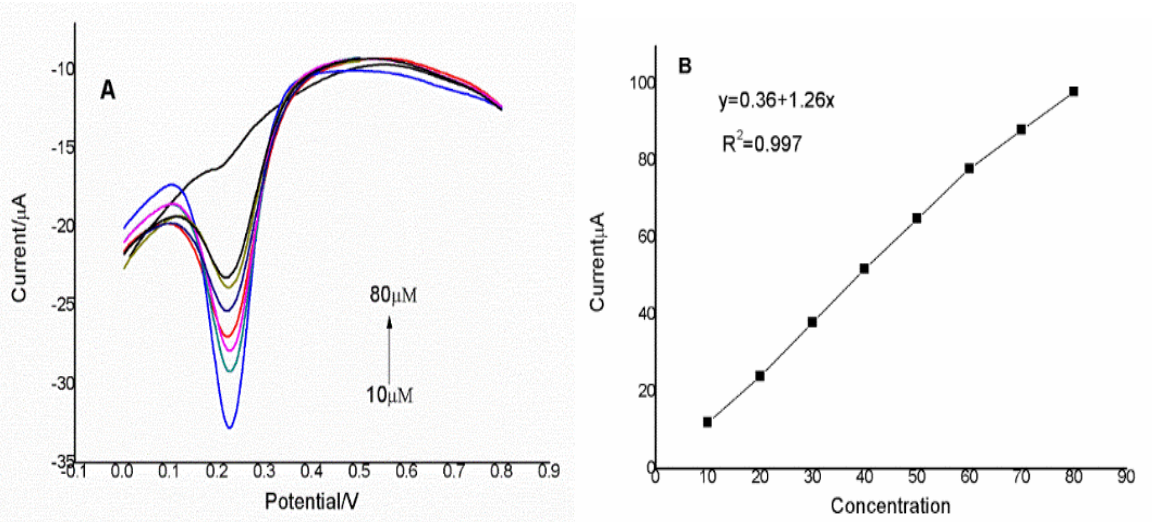

Fig 6**:** (A) Differential pulse voltammograms of the GR/PTh/GCE electrode at varying ibuprofen concentrations (10–80 μM); (B) Calibration curve showing a linear relationship between peak current and ibuprofen concentration, with a detection limit of 1.24 μM.

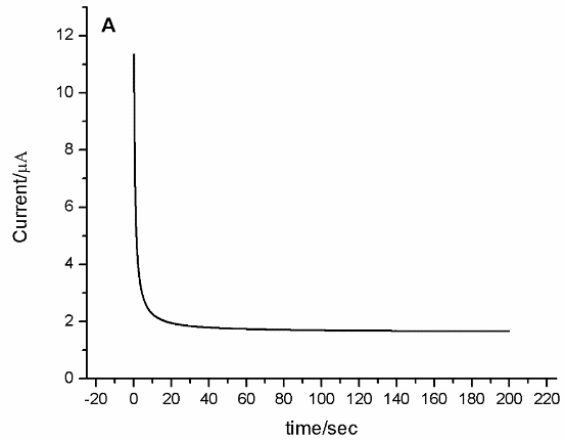

Fig. 7: Current-time (I-t) curve of the GR/PTh/GCE electrode during ibuprofen oxidation, illustrating the influence of accumulation time on the oxidation current, with a significant increase in peak current observed up to 20 seconds of accumulation.

Selectivity and Stability of the electrochemical sensor

In Fig 8, the selectivity and stability of the GR/PTh/GCE electrode for ibuprofen (IBU) detection are investigated. Panel (a) shows the cyclic voltammogram (CV) of the GR/PTh/GCE electrode in the presence of 10 μM ibuprofen, along with potential interference from other compounds, such as Ba^{2+}, Zn^{2+}, Al^{3+}, uric acid, ascorbic acid, and alanine at 100 times the concentration of IBU [45]. The results indicate that none of these species interferes with the oxidation of ibuprofen, as the oxidation peak current continues to increase with the addition of ibuprofen, demonstrating the excellent selectivity of the sensor for IBU detection. Panel (b) illustrates the stability of the modified electrode over time. To evaluate the long-term stability of the GR/PTh/GCE sensor, we extended the storage time to 15 days at 4°C. After 15 days, the electrode retained 90% of its initial peak current when exposed to 10 μM ibuprofen, demonstrating remarkable stability over an extended period. Additionally, to assess the sensor's reusability, the electrode underwent 50 repeated electrochemical cycles using cyclic voltammetry (CV) in a 10 μM ibuprofen solution. The results showed that the electrode retained 85% of its initial current after 50 cycles, indicating excellent reusability and minimal degradation of the electrochemical performance. These findings confirm the GR/PTh/GCE sensor's suitability for long-term use in practical applications, where durability and reusability are crucial [46]. These findings confirm the outstanding selectivity and stability of the GR/PTh/GCE sensor, which is critical for practical applications, particularly in environments where potential interferences are common. The sensor's ability to detect ibuprofen in the presence of other substances without significant loss of performance highlights its potential for real-world applications, such as pharmaceutical analysis and environmental monitoring.

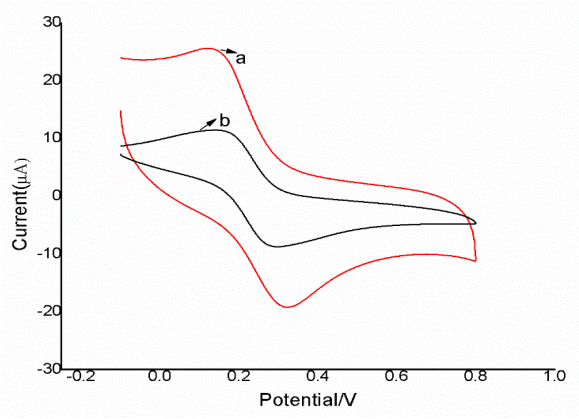

Fig 8**:** (a) Cyclic voltammograms of the GR/PTh/GCE electrode showing the selectivity for ibuprofen (10 μM) in the presence of interferences; (b) Stability of the sensor after 15 days of storage at 4°C, retaining 90% of the original peak current for ibuprofen.

Electroactive Surface Area (ECSA)

The electroactive surface area (ECSA) for bare graphene (GR), polythiophene (PTh), and the GR/PTh composite was calculated using cyclic voltammetry (CV) at various scan rates. The calculated ECSA values for GR, PTh, and GR/PTh were found to be 30 cm^2, 25 cm^2, and 600 cm^2, respectively. The GR/PTh composite exhibited the largest ECSA, which correlates with the enhanced

electrochemical performance observed in the ibuprofen detection experiments. The increased surface area allows for more efficient electron transfer and higher sensitivity for ibuprofen detection. Furthermore, when compared to other existing catalysts, our GR/PTh composite showed a superior electroactive surface area. For example, graphene-polypyrrole (GR/PPy) composites have been reported to have ECSA values of 260 cm^2, while graphene-polyaniline (GR/PANI) composites have values of 512 cm^2 [47]. Our GR/PTh composite outperforms these catalysts, demonstrating its potential as a highly effective material for electrochemical sensors.

Conclusions

In this study, we developed a highly sensitive electrochemical sensor for ibuprofen (IBU) detection using a graphene-polythiophene (GR/PTh) composite-modified glassy carbon electrode. The enhanced electrochemical performance of the GR/PTh composite is attributed to its significantly larger electroactive surface area (ECSA), which provides a greater number of active sites for ibuprofen interaction, resulting in improved sensitivity and a lower detection limit. The calculated ECSA values for GR, PTh, and GR/PTh were found to be 30 cm^2, 25 cm^2, and 600 cm^2, respectively, with the GR/PTh composite exhibiting the largest ECSA. When compared with existing catalysts such as graphene-polypyrrole (GR/PPy) and graphene-polyaniline (GR/PANI) composites, the GR/PTh composite demonstrated a superior ECSA, highlighting its effectiveness for electrochemical applications. This significant improvement in ECSA, combined with the synergistic properties of graphene and polythiophene, underscores the composite's potential for high-performance sensors.

Overall, the study emphasizes the crucial role of ECSA in enhancing sensor performance and offers a promising approach for the development of sensitive electrochemical sensors for pharmaceutical and biomedical applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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