

Article

Polyaniline/Graphitized Carboxylated Multi-Walled Carbon Nanotube Composite Electrode for Highly Sensitive Electrochemical Detection of Pb^{2+} in Seawater

Huahao Tang ¹, Wei Qu ² , Jiahua Su ³ , Muzhi Li ³ and Huili Hao ^{1,4,*} 
¹ Maritime College, Beibu Gulf University, Qinzhou 535011, China

² College of Electronic and Information Engineering, Beibu Gulf University, Qinzhou 535011, China

³ College of Mechanical and Marine Engineering, Beibu Gulf University, Qinzhou 535011, China

⁴ China-ASEAN Smart Port Integrated Hub Technology Innovation College, Beibu Gulf University, Qinzhou 535011, China

* Correspondence: haohuili0022@163.com

Abstract

In this study, an electrochemical sensor based on a graphitized carboxylated multi-walled carbon nanotube/polyaniline (G-COOH-MWCNTs/PANI) composite was developed for the highly sensitive detection of Pb^{2+} in seawater. A G-COOH-MWCNTs/PANI composite dispersion was prepared via a solution blending method and subsequently drop-cast onto a glassy carbon electrode (GCE) to fabricate the modified electrode. Differential pulse anodic stripping voltammetry (DPASV) was employed for the quantitative determination of Pb^{2+} . The morphology of the composite was characterized by scanning electron microscopy (SEM), while the electrochemical behavior of the modified electrode was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Critical experimental parameters, including the type and pH of the supporting electrolyte, deposition potential, deposition time, and loading amount of the composite film, were systematically optimized. In addition, the optimal concentration ratio of G-COOH-MWCNTs to PANI was determined using an orthogonal experimental design. Under the optimized experimental conditions, the proposed sensor exhibited a linear response toward Pb^{2+} over the concentration range of 25–220 $\mu\text{g/L}$, with the regression equation $I_p = 2.757C + 4.316$ ($R^2 = 0.997$). The limit of detection (LOD), calculated at a signal-to-noise ratio (S/N) of 3, was 0.0337 $\mu\text{g/L}$. The sensor also demonstrated excellent reproducibility (relative standard deviation, RSD = 1.7%), satisfactory anti-interference capability, and good long-term stability, retaining 94.1% of its initial response after 35 days of storage. Spike recovery experiments using real seawater samples yielded recoveries ranging from 96.73% to 99.73%, with RSD values below 3%, indicating excellent accuracy and precision in complex seawater matrices. These results demonstrate that the proposed sensor enables accurate determination of Pb^{2+} in seawater without complicated sample pretreatment and exhibits considerable potential for applications in marine environmental monitoring of heavy metal contamination.

Keywords: electrochemical sensor; multi-walled carbon nanotubes; polyaniline; Pb^{2+} ; seawater analysis



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1. Introduction

Lead (Pb) is a highly toxic heavy metal that can enter the human body through inhalation, ingestion, or dermal exposure. Even at extremely low concentrations, Pb can

cause irreversible damage to the nervous, renal, and cardiovascular systems and has been recognized as a potential human carcinogen [1]. With the rapid expansion of industrial activities, the discharge of lead-containing wastewater and the increasing occurrence of marine pollution events have exacerbated lead contamination in seawater [2]. Pb^{2+} can accumulate in marine organisms and be transferred through the food chain, ultimately posing serious threats to both marine ecosystems and human health [3]. Therefore, the development of a simple, highly sensitive, and interference-resistant method for the determination of Pb^{2+} in seawater is of great significance for environmental monitoring and public health protection.

Conventional analytical techniques for Pb^{2+} determination mainly include inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), X-ray fluorescence spectrometry (XRF), and ultraviolet-visible (UV-Vis) spectrophotometry [4,5]. Although these techniques provide excellent sensitivity and analytical accuracy, they generally require expensive instrumentation, complicated operating procedures, and laborious sample pretreatment, making them unsuitable for rapid on-site monitoring, particularly in complex high-salinity matrices such as seawater [6]. Electrochemical sensors have therefore attracted considerable attention as promising alternatives to conventional analytical methods because of their high sensitivity, rapid response, low cost, operational simplicity, and compatibility with miniaturization and portable applications.

The performance of electrochemical sensors is largely determined by the properties of the electrode modification materials. Among various porous carbon materials, multi-walled carbon nanotubes (MWCNTs) have been extensively employed in electrochemical sensing owing to their excellent electrical conductivity, large specific surface area, and remarkable electrochemical activity [7]. However, pristine MWCNTs tend to aggregate because of strong van der Waals interactions and exhibit limited dispersion in aqueous or organic media. Moreover, their lack of specific recognition sites for metal ions significantly restricts their sensing performance [8]. Conductive polyaniline (PANI), featuring high electrical conductivity, reversible redox behavior, and abundant amine and imine functional groups, can interact with carbon nanotubes through π - π conjugation, electrostatic attraction, and coordination interactions to form composite materials with synergistically enhanced properties [9,10]. In such composites, MWCNTs serve as efficient electron acceptors to facilitate charge transport along PANI chains and reduce interfacial resistance [11]. Meanwhile, the incorporation of PANI improves the dispersion stability of MWCNTs while providing abundant binding sites for Pb^{2+} , thereby significantly enhancing the electrochemical response and detection sensitivity of the sensor [12].

PANI/MWCNT-based composites have previously been employed for the electrochemical detection of Pb^{2+} . Shao et al. modified a screen-printed carbon electrode with a gold nanoparticle/PANI-MWCNT composite, enabling the simultaneous determination of Zn^{2+} , Pb^{2+} , and Cu^{2+} , with a detection limit of $0.037 \mu\text{g/L}$ for Pb^{2+} [13]. Siyabonga Shoba et al. fabricated an electrospun nanofibrous composite consisting of PANI, carboxylated MWCNTs (f-MWCNTs), and cobalt phthalocyanine on a gold electrode, achieving a Pb^{2+} detection limit of $0.51 \mu\text{M}$ [14]. Nevertheless, these studies were primarily conducted in purified water or simple buffer systems, whereas investigations involving the determination of Pb^{2+} in complex seawater matrices remain scarce. In seawater, abundant coexisting ions, including Hg^{2+} , Zn^{2+} , Cu^{2+} , and Cd^{2+} , may compete for active adsorption sites on the electrode surface and alter the interfacial electrical double-layer structure as well as the mass-transfer behavior of target ions, thereby reducing detection sensitivity and causing signal instability. Consequently, developing a PANI/MWCNT-based electrochemical sensor capable of highly sensitive and selective Pb^{2+} detection in seawater remains both scientifically significant and practically important.

Motivated by these considerations, graphitized carboxylated multi-walled carbon nanotubes (G-COOH-MWCNTs) and polyaniline (PANI) were employed to fabricate a G-COOH-MWCNTs/PANI composite via a solution blending method. The resulting composite was drop-cast onto a glassy carbon electrode to construct an electrochemical sensing platform for Pb^{2+} determination in seawater. The morphology and electrochemical properties of the composite were systematically characterized. Key analytical parameters, including the pH of the supporting electrolyte, deposition potential, deposition time, and composite loading amount, were optimized, while the interactions among multiple factors were evaluated using an orthogonal experimental design. Under the optimized conditions, a calibration curve for Pb^{2+} determination was established, and the reproducibility, long-term stability, and anti-interference performance of the sensor were comprehensively evaluated. Furthermore, the practical applicability and analytical reliability of the proposed sensor were verified through spike recovery experiments using real seawater samples. This work provides a feasible electrochemical sensing strategy for the rapid and accurate determination of trace Pb^{2+} in marine environments.

2. Experimental

2.1. Reagents and Instruments

Graphitized carboxylated multi-walled carbon nanotubes (G-COOH-MWCNTs; purity >99.9%, outer diameter: 10–20 nm, length: 5–30 μm), acetate buffer solution (HAc–NaAc), potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$, purity $\geq 99.95\%$), and phosphate-buffered saline (PBS) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Polyaniline (PANI; particle size: 3–100 μm) was obtained from Beijing Bailingwei Technology Co., Ltd. (Beijing, China). All chemicals were of analytical reagent (AR) or guaranteed reagent (GR) grade and were used without further purification. Ultrapure water with a resistivity of 18.0 $\text{M}\Omega\cdot\text{cm}$ was used throughout the experiments. Seawater samples were collected from the Sanniang Bay coastal area (Dafengjiang Sea Area), Qinzhou, Guangxi, China.

Electrochemical measurements were performed using a CHI660E electrochemical workstation (CH Instruments, Shanghai, China). The morphology of the materials was characterized using a Quattro S scanning electron microscope (Thermo Fisher Scientific, Guangzhou, China). Other instruments included an LC-101-0B electric blast drying oven, an FA124 external calibration analytical balance, an LC-LX-H165A high-speed centrifuge, a DF-101S magnetic stirrer, and an LC-LX-H165A ultrasonic cleaner (Lichen Instrument Technology Co., Ltd., Shanghai, China). Ultrapure water was supplied by a PLUSE2-5TH ultrapure water purification system (EPED Technology Co., Ltd., Nanjing, China).

2.2. Experimental Procedures

2.2.1. Preparation of the G-COOH-MWCNTs/PANI Composite Dispersion

Briefly, 10.0 mg of G-COOH-MWCNTs and 5.0 mg of PANI were accurately weighed and transferred into a clean 10 mL glass vial. Subsequently, 5.0 mL of *N,N*-dimethylformamide (DMF) was added as the dispersing solvent. After sealing, the mixture was ultrasonicated for 60 min until a homogeneous and stable black suspension was obtained. The resulting dispersion contained G-COOH-MWCNTs and PANI at concentrations of 2.0 and 1.0 mg/mL, respectively, corresponding to a total solid concentration of 3.0 mg/mL. The prepared dispersion was stored at room temperature, and ultrasonicated again for 15 min before use to ensure uniform redispersion.

2.2.2. Fabrication of the Modified Electrode

A glassy carbon electrode (GCE, 3 mm in diameter) was sequentially polished on a polishing cloth using alumina slurries with particle sizes of 1.0, 0.3, and 0.05 μm until

a mirror-like surface was obtained. The polished electrode was then thoroughly rinsed with absolute ethanol and ultrapure water for 3 min each to remove residual alumina particles and organic contaminants. After cleaning, the electrode was naturally dried at room temperature before modification.

The modified electrode was prepared using a drop-casting method. Briefly, 5.0 μL of the G-COOH-MWCNTs/PANI composite dispersion was uniformly drop-cast onto the surface of the pretreated GCE. The electrode was then dried at 25 $^{\circ}\text{C}$ in a drying oven to allow complete evaporation of the solvent, forming a uniform composite film on the electrode surface. The resulting modified electrode was denoted as G-COOH-MWCNTs/PANI/GCE. For comparison, a G-COOH-MWCNTs-modified electrode (G-COOH-MWCNTs/GCE) was prepared using the same procedure, with the concentration of the nanotube dispersion identical to that used in the composite system. All modified electrodes were stored at 4 $^{\circ}\text{C}$ before use.

2.2.3. Electrochemical Measurements

The electrochemical determination of Pb^{2+} was carried out using differential pulse anodic stripping voltammetry (DPASV) according to the reported procedure [15]. A conventional three-electrode system was employed, consisting of the G-COOH-MWCNTs/PANI/GCE as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the counter electrode. The experimental parameters of DPASV are listed in Table 1.

Table 1. Main parameters of differential pulse voltammetry.

Parameter	Numerical Value	Unit
Inct E	0.004	V
Amplitude	0.05	V
Pulse Width	0.05	s
Sampling Width	0.0167	s
Pulse Period	0.5	s
Quiet Time	2	s

For each measurement, an appropriate volume of Pb^{2+} standard solution was transferred into an electrochemical cell, followed by the addition of acetate buffer (HAc–NaAc) to obtain a final solution volume of 10.0 mL. Under an applied deposition potential, the solution was magnetically stirred to facilitate the accumulation of Pb^{2+} onto the modified electrode surface through electrostatic attraction and coordination interactions. After the deposition step, stirring was stopped and the solution was allowed to stand for 10 s to establish equilibrium before DPASV measurements were performed under the optimized operating conditions.

A well-defined and symmetric stripping peak was observed at approximately -0.5 V, corresponding to the anodic stripping oxidation of deposited Pb. The stripping peak current increased linearly with increasing Pb^{2+} concentration and was therefore used as the analytical signal for quantitative determination. After each measurement, the modified electrode was transferred into a blank buffer solution and electrochemically cleaned at $+0.6$ V under magnetic stirring for 120 s to completely remove residual Pb and deposited species from the electrode surface, ensuring good reusability. All electrochemical experiments were carried out at room temperature, and each measurement was performed in triplicate. The results are presented as the mean $\pm$ standard deviation (SD).

3. Results and Discussion

3.1. Morphological and Electrochemical Characterization of the Modified Materials

The surface morphologies of G-COOH-MWCNTs, PANI, and the G-COOH-MWCNTs/PANI composite were characterized by scanning electron microscopy (SEM) [16]. Representative SEM images of the three materials at magnifications of 50,000 $\times$ and 150,000 $\times$ are presented in Figure 1.

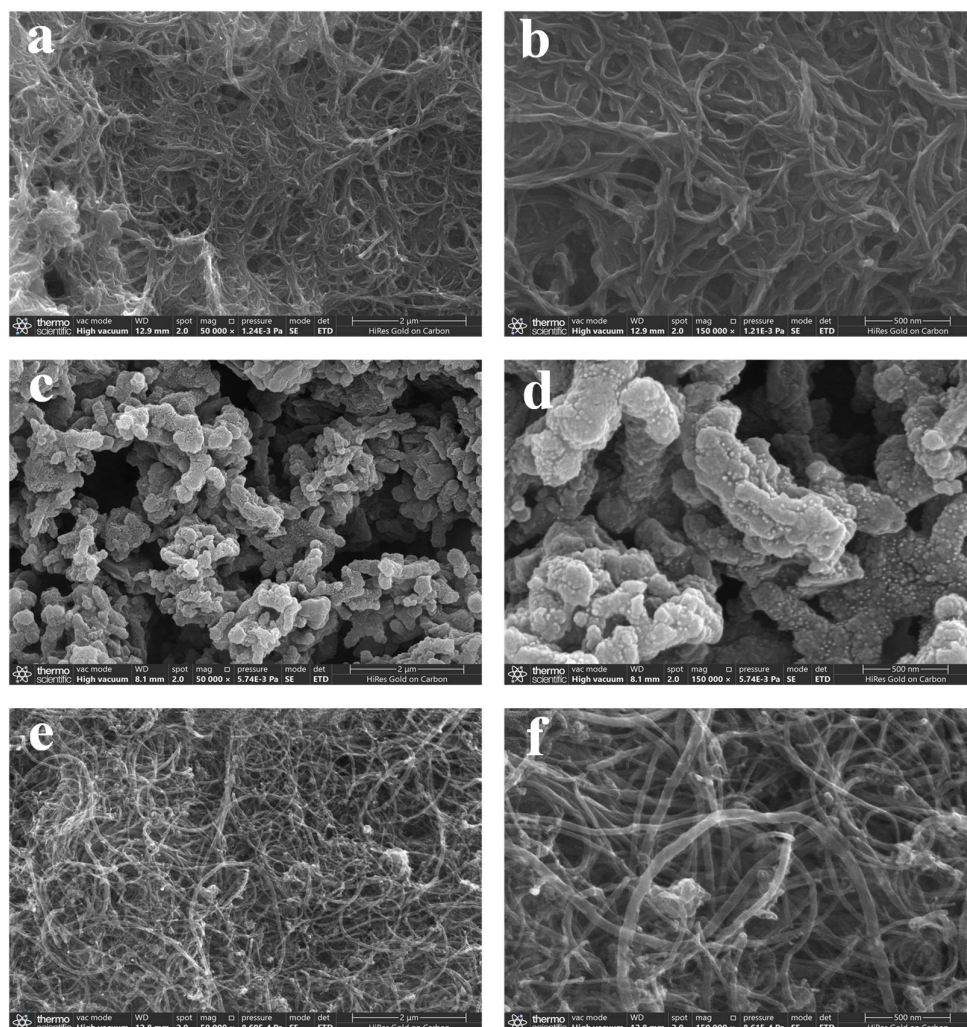


Figure 1. SEM images of G-COOH-MWCNTs (a,b), PANI (c,d), and the G-COOH-MWCNTs/PANI composite (e,f).

The morphology of G-COOH-MWCNTs is shown in Figure 1a,b. The G-COOH-MWCNTs exhibited a typical tubular fibrous structure, in which individual nanotubes were randomly intertwined to form a loose and porous three-dimensional network. At higher magnification (Figure 1b), the tubular walls of individual nanotubes were clearly distinguishable, with relatively uniform tube diameters. The nanotubes were well dispersed, although a small number of aggregates were observed.

The morphology of PANI is presented in Figure 1c,d. PANI exhibited irregular granular and short rod-like structures with a broad particle size distribution. The particles were densely packed, and localized agglomerates formed through particle stacking were observed. Compared with G-COOH-MWCNTs, the PANI surface was relatively rough and no obvious porous structure was detected.

The morphology of the G-COOH-MWCNTs/PANI composite is shown in Figure 1e,f. In the composite, PANI particles were uniformly attached to the outer surfaces and intersti-

tial regions of the G-COOH-MWCNTs. Although the tubular morphology of the carbon nanotubes remained distinguishable, the nanotube surfaces became noticeably rougher, and partial coating of the nanotubes by PANI was observed. Compared with pristine G-COOH-MWCNTs, the interconnected nanotube network was largely preserved while forming a denser composite film. Moreover, the number of nanotube aggregates was significantly reduced, indicating a marked improvement in dispersion uniformity. This improvement can be attributed to the incorporation of PANI, which effectively suppressed the van der Waals interactions between adjacent nanotubes [17] and thereby enhanced their dispersion within the composite system [18]. No obvious phase separation between PANI and G-COOH-MWCNTs was observed, suggesting excellent interfacial compatibility between the two components.

3.2. Electrochemical Behavior of the Modified Electrodes

The electrochemical behavior of the G-COOH-MWCNTs/PANI-modified electrode and the synergistic effect of the composite material were investigated by cyclic voltammetry (CV) [19] and differential pulse voltammetry (DPV) [15]. Figure 2a compares the CV curves of the bare GCE, G-COOH-MWCNTs/GCE, and G-COOH-MWCNTs/PANI/GCE recorded in acetate buffer (pH 5.5) containing 5 $\mu\text{g/L}$ Pb^{2+} .

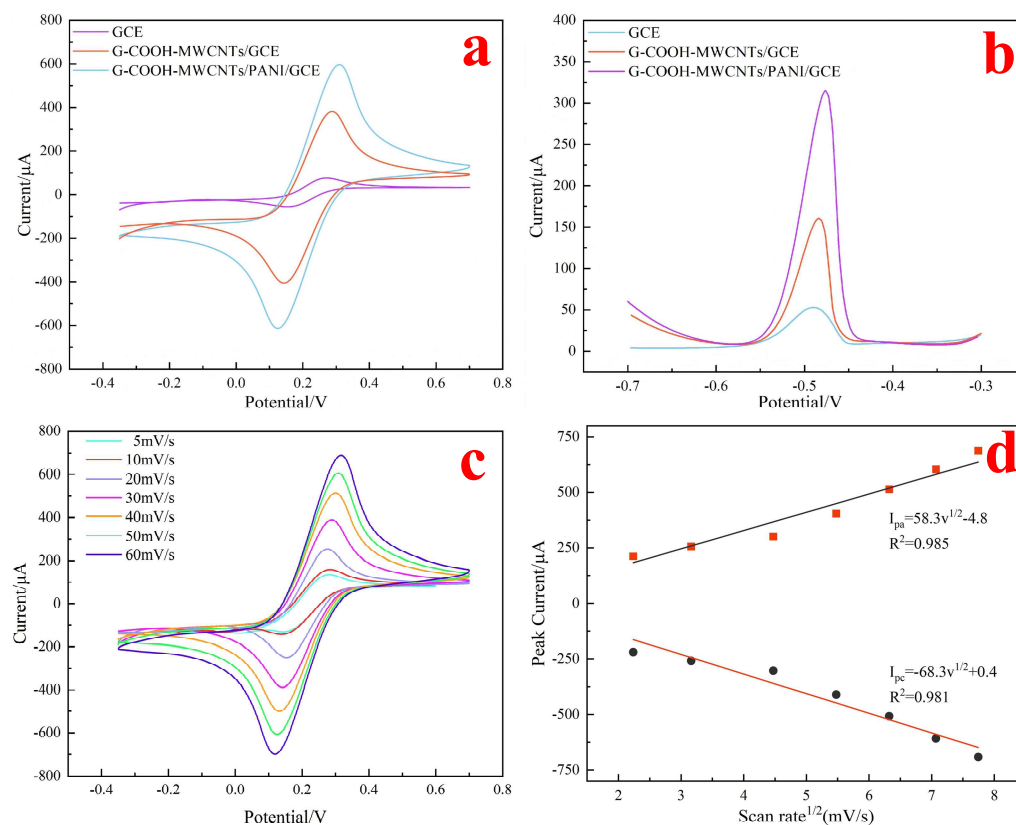


Figure 2. Electrochemical characterization of G-COOH-MWCNTs/PANI/GCE: (a) comparison of CV curves obtained with different modified electrodes; (b) comparison of DPV curves obtained with different modified electrodes; (c) CV curves recorded at different scan rates; and (d) linear relationships between peak current and the square root of the scan rate.

As shown in Figure 2a, the bare GCE exhibited only weak redox peaks over the potential range from -0.4 to 0.8 V, with a background current of approximately -50 μA . After modification with G-COOH-MWCNTs, a well-defined pair of redox peaks appeared. The anodic peak was located at approximately 0.3 V with a peak current of about 380 μA , while the corresponding cathodic peak appeared at approximately 0.1 V with a peak current of ap-

proximately $-400\ \mu\text{A}$, demonstrating the excellent electrical conductivity and electrochemical activity of the G-COOH-MWCNTs layer. For the G-COOH-MWCNTs/PANI/GCE, the anodic peak current increased markedly to approximately $620\ \mu\text{A}$, whereas the cathodic peak current increased to approximately $-610\ \mu\text{A}$, corresponding to approximately 1.5 times those obtained with G-COOH-MWCNTs/GCE. The substantial enhancement in peak currents indicates that the incorporation of PANI effectively improved both the interfacial charge-transfer efficiency and the electrochemically active surface area. In addition, the oxidation peak became sharper and more symmetrical, suggesting that the synergistic interaction between G-COOH-MWCNTs and PANI facilitated charge-transfer kinetics at the electrode/electrolyte interface [20].

The corresponding DPV responses of the three electrodes under identical experimental conditions are presented in Figure 2b. A weak stripping peak with a current of approximately $50\ \mu\text{A}$ was observed near $-0.5\ \text{V}$ for the bare GCE, indicating only a limited electrochemical response toward Pb^{2+} . After modification with G-COOH-MWCNTs, the stripping peak current increased to approximately $150\ \mu\text{A}$, demonstrating the enhanced accumulation capability of the nanotube-modified electrode. In contrast, G-COOH-MWCNTs/PANI/GCE exhibited a substantially enhanced stripping peak with a current of approximately $320\ \mu\text{A}$, which was about twice that of G-COOH-MWCNTs/GCE. This remarkable enhancement can be attributed to the synergistic effects of the composite components. On the one hand, the three-dimensional network structure of G-COOH-MWCNTs provides a large electroactive surface area and efficient electron-transport pathways for Pb^{2+} accumulation [21]. On the other hand, the abundant amine and imine functional groups in PANI effectively coordinate with Pb^{2+} , thereby improving the enrichment efficiency of the target ions at the electrode surface. The combination of these effects significantly enhances the electrochemical sensitivity of the sensor toward Pb^{2+} [22].

The CV and DPV results collectively demonstrate that the synergistic interaction between G-COOH-MWCNTs and PANI substantially improves the sensing performance of the electrode, indicating its suitability for the quantitative determination of Pb^{2+} .

To further investigate the electrode reaction kinetics of G-COOH-MWCNTs/PANI/GCE, CV measurements were carried out in a solution containing $5\ \text{mM}\ \text{K}_3[\text{Fe}(\text{CN})_6]$ and $0.1\ \text{M}\ \text{KCl}$ at scan rates ranging from 5 to $60\ \text{mV/s}$. The influence of scan rate on the electrochemical behavior of the modified electrode is shown in Figure 2c and the parameters are shown in Table 2. As the scan rate increased from 5 to $60\ \text{mV/s}$, both the anodic peak current (I_{pa}) and cathodic peak current (I_{pc}) increased progressively. Meanwhile, the anodic peak potential (E_{pa}) shifted slightly toward more positive potentials, whereas the cathodic peak potential (E_{pc}) shifted slightly toward more negative potentials, indicating that the electrode process was jointly influenced by charge-transfer kinetics and mass transport [23].

Table 2. Summary of cyclic voltammetric parameters of the G-COOH-MWCNTs/PANI/GCE at different scan rates.

Scanning Speed/mV	I_{pa}	I_{pc}	$ I_{\text{pa}}/I_{\text{pc}} $
5	135.87	-131.32	1.03
10	142.02	-157.74	0.90
20	252.89	-249.40	1.01
30	390.26	-384.24	1.02
40	513.07	-491.63	1.04
50	603.79	-610.71	0.98
60	687.02	-709.48	0.96

Linear regression analysis was performed by plotting I_{pa} and I_{pc} against the square root of the scan rate ($v^{1/2}$), and the corresponding results are presented in Figure 2d [24,25]. Good linear relationships were obtained over the scan rate range of 5–60 mV/s. The regression equations were $I_{pa} (\mu A) = 58.3v^{1/2} - 4.8$ ($R^2 = 0.985$) and $I_{pc} (\mu A) = -68.3v^{1/2} + 0.4$ ($R^2 = 0.981$), respectively.

The Randles-Sevcik equation was employed to quantitatively estimate the effective electroactive surface area (A) of the electrodes, based on the linear relationship between peak current and the square root of the scan rate in the ferricyanide probe:

$$I_p = 2.69 \times 10^5 A D^{\frac{1}{2}} n^{\frac{3}{2}} v^{\frac{1}{2}} c \quad (1)$$

where I_p is the peak current (μA , using the average of $|I_{pa}|$ and $|I_{pc}|$), A is the effective surface area (cm^2), D is the diffusion coefficient (cm^2/s , taken as $7.6 \times 10^{-6} cm^2/s$), n is the number of electrons transferred ($n = 1$), v is the scan rate (V/s , $v = 0.05 V/s$), and c is the concentration of $K_3Fe(CN)_6$ (mM , $c = 5 mM$). The calculated effective areas were: GCE ($0.07 cm^2$), G-COOHMWCNTs/GCE ($0.21 cm^2$), and G-COOHMWCNTs/PANI/GCE ($0.30 cm^2$). The effective area of M-COOH-MWCNTs/PANI/GCE is significantly larger than that of the bare GCE, indicating that the synergistic combination of PANI and M-COOH-MWCNTs significantly expands the electroactive surface.

3.3. Optimization of Experimental Conditions

3.3.1. Optimization of the Supporting Electrolyte and pH

The type and pH of the supporting electrolyte play crucial roles in determining the electrochemical performance of the sensor, as they influence the ionic strength of the solution, the chemical speciation of the target ions, and the interfacial charge state of the electrode, thereby affecting the accumulation efficiency and stripping response of Pb^{2+} on the modified electrode surface [26–28]. In this study, five commonly used supporting electrolytes, including phosphate-buffered saline (PBS), KCl, HNO_3 , acetate buffer (HAc–NaAc), and H_2SO_4 , as well as different pH values (4.0, 4.5, 5.0, 5.5, and 6.0), were systematically investigated to determine the optimum detection conditions.

1. Selection of the Supporting Electrolyte

The representative DPV curves recorded in different supporting electrolytes (all adjusted to pH 5.0) are shown in Figure 3a, while the corresponding stripping peak currents obtained from three parallel measurements are summarized in Figure 3b. As shown in Figure 3a, the stripping peak of Pb^{2+} appeared at approximately $-0.5 V$ in all electrolyte systems, indicating that the type of supporting electrolyte had little influence on the stripping peak potential. However, the stripping peak current varied considerably among the different electrolytes (Figure 3b). The highest peak current, approximately $380 \mu A$, was obtained in the HAc–NaAc buffer, followed by H_2SO_4 (approximately $230 \mu A$) and HNO_3 (approximately $170 \mu A$), whereas considerably lower responses were observed in PBS and KCl, with peak currents of approximately 125 and $120 \mu A$, respectively. The superior performance of the HAc–NaAc buffer can be attributed to two factors. First, the acetate buffer possesses an appropriate ionic strength and excellent buffering capacity, which effectively maintains a stable solution pH during the electrochemical process [29]. Second, weak coordination interactions between Pb^{2+} and acetate ions may facilitate the preconcentration of Pb^{2+} on the electrode surface, thereby enhancing the stripping response [30]. Therefore, HAc–NaAc buffer was selected as the optimal supporting electrolyte for subsequent experiments.

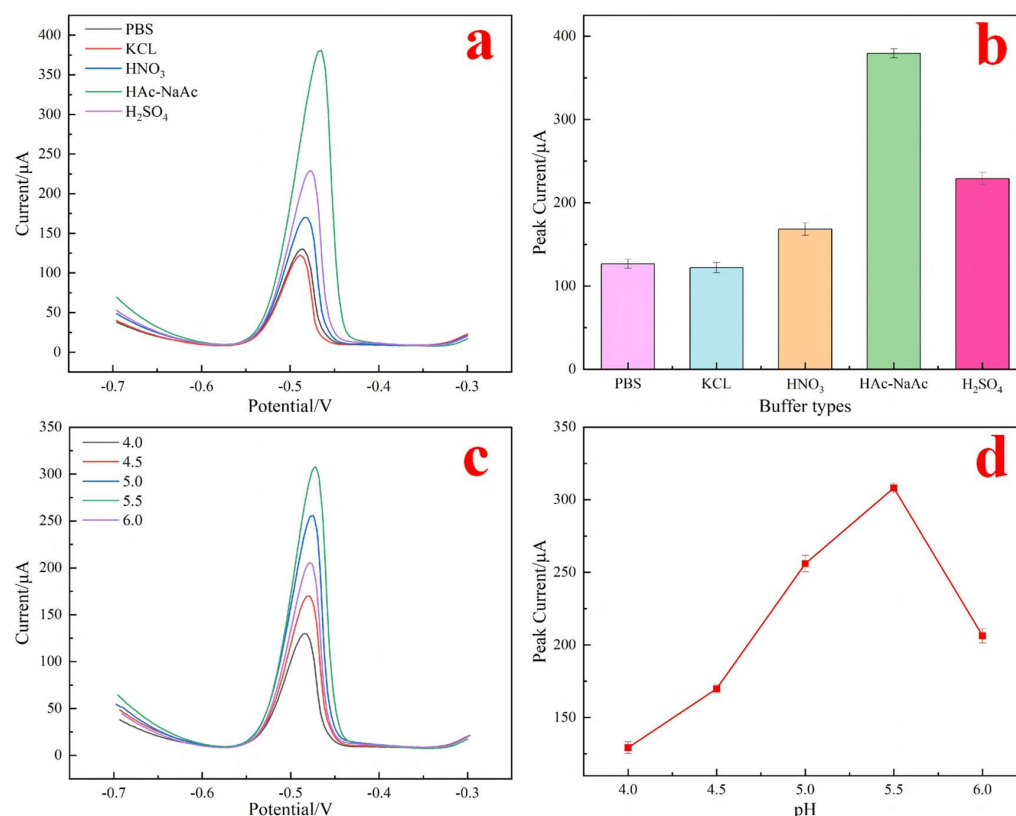


Figure 3. DPV responses of G-COOH-MWCNTs/PANI/GCE obtained in (a) different supporting electrolytes (pH 5.0) and (c) HAC-NaAc buffer with different pH values; (b,d) corresponding stripping peak currents (mean $\pm$ SD, $n = 3$). All measurements were carried out in solution containing 150 μ g/L Pb²⁺.

2. Optimization of the Buffer pH

After selecting HAC-NaAc as the supporting electrolyte, the influence of pH on the stripping response of Pb²⁺ was further investigated over the pH range of 4.0–6.0. The corresponding DPV curves and the variation in stripping peak current with pH are shown in Figure 3c,d, respectively.

As shown in Figure 3d, the stripping peak current increased continuously as the pH increased from 4.0 to 5.5, reaching a maximum value of approximately 310 μ A at pH 5.5. A further increase in pH to 6.0 resulted in a pronounced decrease in peak current to approximately 205 μ A. The initial increase in current can be attributed to the gradual reduction in proton concentration. At relatively low pH (<5.5), excessive H⁺ ions compete with Pb²⁺ for active binding sites on the electrode surface, while the hydrogen evolution reaction may further interfere with the electrodeposition process, thereby suppressing Pb²⁺ accumulation. In contrast, at higher pH values (>5.5), Pb²⁺ undergoes hydrolysis to form hydroxyl complexes such as Pb(OH)⁺ and Pb(OH)₂, reducing the concentration of free Pb²⁺ available for electrodeposition and consequently decreasing the stripping signal [31]. Based on these results, pH 5.5 was selected as the optimal operating condition.

3.3.2. Optimization of the Deposition Potential and Deposition Time

The deposition potential and deposition time are two critical parameters in differential pulse anodic stripping voltammetry (DPASV), as they determine the amount of metallic Pb deposited on the electrode surface and consequently affect the stripping signal. Therefore, both parameters were systematically optimized.

1. Optimization of the Deposition Potential

The effect of deposition potential was investigated over the range from -0.8 to -1.2 V while maintaining a constant deposition time of 180 s. The DPV responses and the corresponding stripping peak currents are shown in Figure 4a,b, respectively.

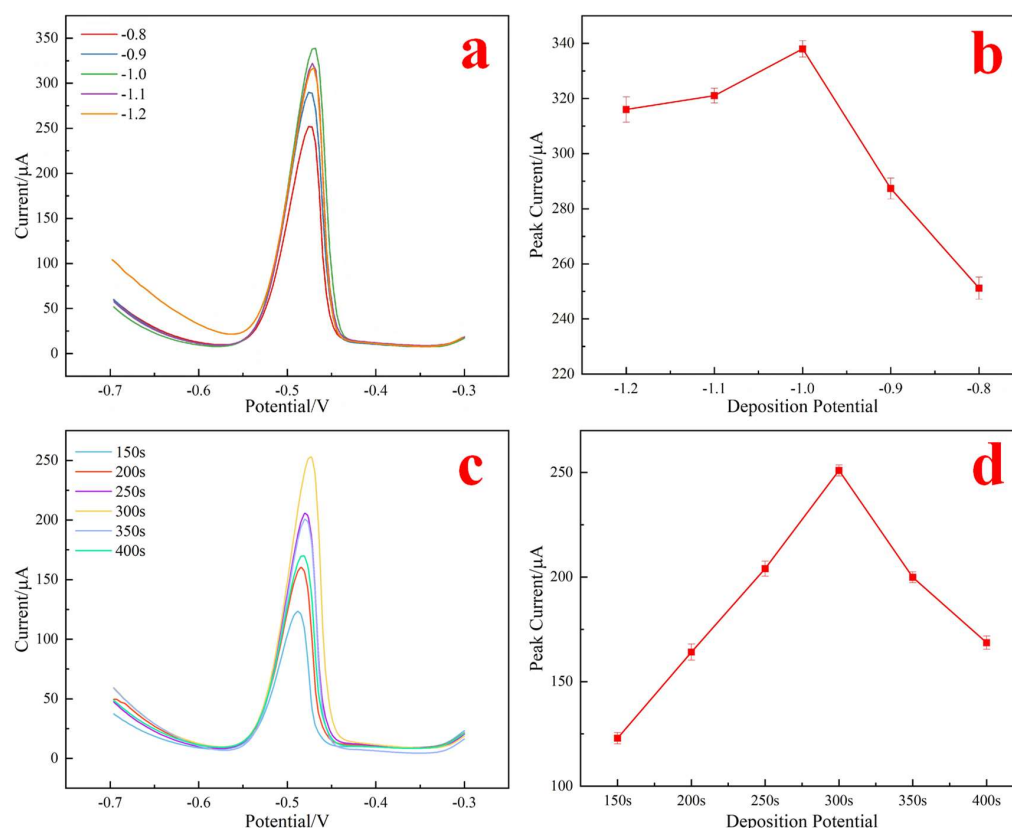


Figure 4. DPV responses of G-COOH-MWCNTs/PANI/GCE obtained at different (a) deposition potentials and (c) deposition times; (b,d) corresponding stripping peak currents (mean $\pm$ SD, $n = 3$). All measurements were carried out in solution containing 150 $\mu\text{g/L}$ Pb²⁺.

As shown in Figure 4a, well-defined and symmetric stripping peaks were observed at approximately -0.5 V under all deposition potentials investigated. As illustrated in Figure 4b, the stripping peak current increased markedly from approximately 250 μA at -0.8 V to approximately 338 μA at -1.0 V, where the maximum response was obtained. Further shifting the deposition potential to -1.1 and -1.2 V caused the peak current to decrease slightly to approximately 320 and 315 μA , respectively.

The observed trend can be explained by the deposition mechanism. At less negative potentials, the driving force for the electrochemical reduction in Pb²⁺ is insufficient, resulting in incomplete electrodeposition. Conversely, excessively negative potentials promote the hydrogen evolution reaction, which interferes with the uniform deposition of metallic Pb and consequently reduces the stripping response [32]. Therefore, -1.0 V was selected as the optimum deposition potential.

2. Optimization of the Deposition Time

The influence of deposition time was subsequently evaluated over the range of 150–400 s under the optimized deposition potential. The corresponding DPV curves and stripping peak currents are presented in Figure 4c,d.

The stripping peak current increased gradually from approximately 120 μA at 150 s to approximately 250 μA at 300 s, indicating that longer deposition times promoted the accumulation of Pb²⁺ on the electrode surface. However, when the deposition time was

further extended to 350 and 400 s, the peak current decreased to approximately 200 and 160 μA , respectively.

This behavior can be attributed to the progressive occupation of active sites during the deposition process. At shorter deposition times, abundant active sites are available, allowing continuous electrodeposition of Pb^{2+} . In contrast, prolonged deposition results in the formation of an excessively thick Pb layer, which hinders mass transport and electron transfer, thereby decreasing the stripping efficiency. Consequently, a deposition time of 300 s was selected for subsequent experiments.

Overall, the optimum deposition potential and deposition time were determined to be -1.0 V and 300 s, respectively.

3.3.3. Optimization of the Composite Film Loading

The amount of modifier deposited on the electrode surface directly influences the number of electroactive sites and the interfacial charge-transfer characteristics of the sensor [28]. Under the optimized conditions, namely HAc–NaAc buffer (pH 5.5), a deposition potential of -1.0 V , and a deposition time of 300 s, the effect of the loading amount of the G-COOH-MWCNTs/PANI composite dispersion was investigated over the range of 2–7 μL .

As shown in Figure 5, the stripping peak current increased steadily from approximately 300 μA to approximately 380 μA as the loading volume increased from 2 to 5 μL . However, a further increase in the loading volume to 6 and 7 μL resulted in a gradual decrease in the stripping peak current.

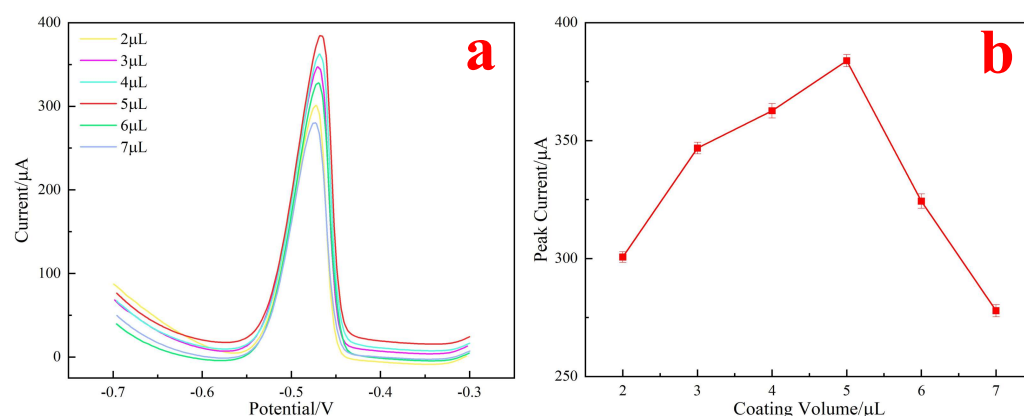


Figure 5. (a) DPV responses of G-COOH-MWCNTs/PANI/GCE prepared with different composite film loadings; (b) corresponding stripping peak currents as a function of film loading (mean $\pm$ SD, $n = 3$). All measurements were carried out in solution containing 150 $\mu\text{g/L}$ Pb^{2+} .

The initial increase in peak current is attributed to the increased number of electroactive sites provided by the larger amount of composite material, which enhances the accumulation of Pb^{2+} . In contrast, excessive film loading produces a thicker modification layer that increases the interfacial resistance and impedes electron transfer, thereby reducing the electrochemical response. Accordingly, a loading volume of 5 μL was selected as the optimum amount of the composite film.

3.3.4. Optimization of the Composite Composition by Orthogonal Experimental Design

Based on the results of the single-factor optimization experiments, an orthogonal experimental design was further employed to investigate the combined effects of the concentrations of G-COOH-MWCNTs and PANI on the electrochemical response and to determine the optimal composition of the composite dispersion. An L_9 (3^2) orthogonal array, consisting of two factors at three levels, was adopted for multivariate optimization.

The concentration of PANI (Factor A: 0.7, 1.0, and 1.3 mg/mL) and the concentration of G-COOH-MWCNTs (Factor B: 1.7, 2.0, and 2.3 mg/mL) were selected as the experimental variables, while the stripping peak current was used as the evaluation index. According to the orthogonal array design, nine sets of experiments were conducted. For each set, the average value obtained from three independent electrodes of the same batch was used. The experimental design and corresponding results are summarized in Table 3.

Table 3. Orthogonal experimental design and results for different concentration combinations of PANI and G-COOH-MWCNTs.

No	PANI	G-COOH-MWCNTs	Peak Current	RSD
	(mg/mL)	(mg/mL)	(μ A)	
1	0.7	1.7	313.8	1.21%
2	0.7	2.0	331.4	2.04%
3	0.7	2.3	346.2	0.98%
4	1.0	1.7	348.7	1.17%
5	1.0	2.0	355.2	2.01%
6	1.0	2.3	350.1	1.63%
7	1.3	1.7	328.8	1.14%
8	1.3	2.0	328.9	1.01%
9	1.3	2.3	349.2	0.85%

As shown in Table 3, the stripping peak currents obtained from the nine experimental combinations ranged from 313.8 to 355.2 μ A. Among them, Experiment 5, corresponding to 1.0 mg/mL PANI and 2.0 mg/mL G-COOH-MWCNTs, exhibited the highest stripping peak current of 355.2 μ A, whereas Experiment 1, containing 0.7 mg/mL PANI and 1.7 mg/mL G-COOH-MWCNTs, produced the lowest response of 313.8 μ A. These results indicate that an insufficient PANI concentration provides an inadequate number of active binding sites on the electrode surface, thereby limiting the enrichment efficiency of Pb^{2+} [31]. In contrast, an appropriate combination of PANI and G-COOH-MWCNTs effectively exploits the synergistic enrichment effect of the two components.

To quantitatively evaluate the influence of each factor, the average stripping peak current at each factor level and the corresponding range (*R*) values were calculated, as summarized in Table 4. The range value for the PANI concentration was 20.8, whereas that for the G-COOH-MWCNTs concentration was 18.1. Since $R_{PANI} > R_{G-COOH-MWCNTs}$, the concentration of PANI exerted a slightly greater influence on the electrochemical response within the investigated concentration range, indicating that PANI is the dominant factor governing sensor performance. This observation is consistent with the sensing mechanism, as the abundant amine and imine functional groups along the PANI molecular chains serve as the primary recognition and coordination sites for Pb^{2+} . Consequently, variations in the PANI concentration directly affect the number of active binding sites available on the electrode surface and thus have a more pronounced influence on the enrichment efficiency.

Table 4. Average stripping peak currents and range analysis for different concentration levels of PANI and G-COOH-MWCNTs.

Average	PANI	Average	G-COOH-MWCNTs	Average
	(mg/mL)	(μ A)	(mg/mL)	(μ A)
Average 1	0.7	330.5	1.7	330.4
Average 2	1.0	351.3	2.0	338.5
Average 3	1.3	335.4	2.3	348.5
Range	—	20.8	—	18.1

According to the average responses at each factor level (Table 4), the optimal concentrations were determined to be 1.0 mg/mL for PANI ($K_2 = 351.3 \mu\text{A}$) and 2.3 mg/mL for G-COOH-MWCNTs ($K_3 = 348.5 \mu\text{A}$). Considering both the range analysis and the experimental results shown in Table 3, Experiment 5 (1.0 mg/mL PANI + 2.0 mg/mL G-COOH-MWCNTs) yielded the highest stripping peak current ($355.2 \mu\text{A}$), which was generally consistent with the statistical analysis. Therefore, the optimal composition of the composite dispersion was determined to be 1.0 mg/mL PANI and 2.0 mg/mL G-COOH-MWCNTs.

3.4. Linear Range and Limit of Detection

Under the optimized experimental conditions, namely HAc–NaAc buffer (pH 5.5), a deposition potential of -1.0 V , a deposition time of 300 s, and a composite film loading of $5 \mu\text{L}$, the analytical performance of G-COOH-MWCNTs/PANI/GCE toward Pb^{2+} was evaluated by DPV. The DPV responses obtained for different concentrations of Pb^{2+} are presented in Figure 6a, while the corresponding calibration curve is shown in Figure 6b.

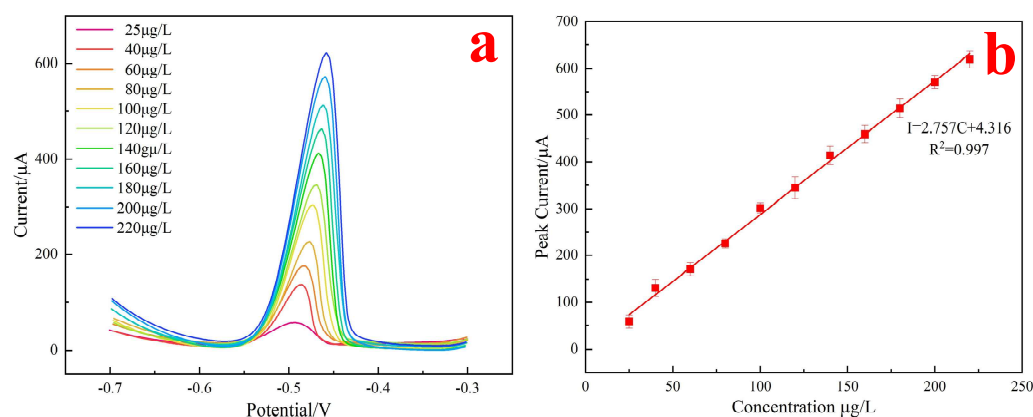


Figure 6. (a) DPV responses of G-COOH-MWCNTs/PANI/GCE toward different concentrations of Pb^{2+} ; (b) calibration curve showing the relationship between stripping peak current and Pb^{2+} concentration ($n = 3$).

As shown in Figure 6a, the stripping peak current increased progressively as the Pb^{2+} concentration increased from 25 to 225 $\mu\text{g/L}$. In all cases, a well-defined stripping peak appeared at approximately -0.5 V . At relatively low Pb^{2+} concentrations, abundant active sites were available on the electrode surface, resulting in a rapid increase in stripping peak current with increasing analyte concentration. As the concentration increased further, the active sites gradually approached saturation, leading to a slower increase in the peak current.

As illustrated in Figure 6b, an excellent linear relationship was obtained between the stripping peak current and Pb^{2+} concentration over the range of 25–220 $\mu\text{g/L}$. The corresponding linear regression equation was: $I_p = 2.757C + 4.316$ ($R^2 = 0.997$), where I_p is the stripping peak current (μA) and C is the Pb^{2+} concentration ($\mu\text{g/L}$). To determine the limit of detection (LOD), the modified electrode was tested in a blank solution under identical experimental conditions for eleven consecutive measurements. The standard deviation (SD) of the blank response was calculated to be $0.031 \mu\text{A}$.

According to the $3S/N$ criterion, the LOD was calculated using the following equation [15]:

$$\text{LOD} = 3SD/K \quad (2)$$

where SD is the standard deviation of the blank response and K is the slope of the calibration curve. Based on this equation, the LOD of the proposed sensor was calculated to be $0.0337 \mu\text{g/L}$.

3.5. Reproducibility, Anti-Interference Capability, and Stability of the Sensor

Reproducibility, selectivity, and long-term stability are essential performance indicators for evaluating the practical applicability of electrochemical sensors. These characteristics of G-COOH-MWCNTs/PANI/GCE were systematically investigated, and the results are presented in Figure 7.

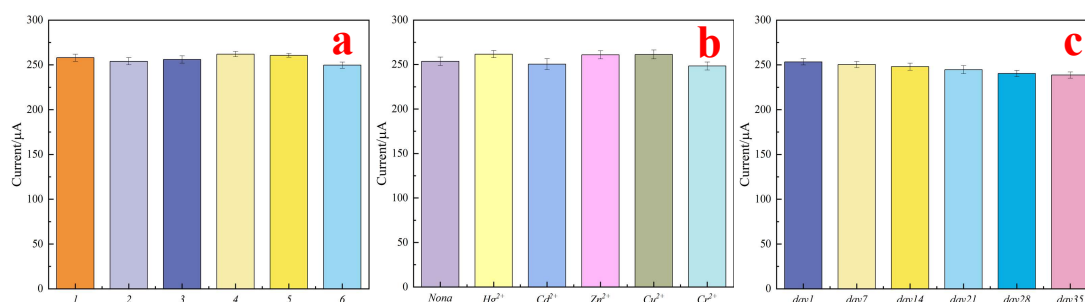


Figure 7. Performance evaluation of G-COOH-MWCNTs/PANI/GCE: (a) reproducibility ($n = 6$); (b) anti-interference capability toward common coexisting metal ions; and (c) long-term storage stability over 35 days.

1. Reproducibility

Six G-COOH-MWCNTs/PANI/GCE electrodes were independently fabricated under identical preparation conditions and used to detect $100 \mu\text{g/L Pb}^{2+}$ under the optimized experimental conditions. As shown in Figure 7a, the stripping peak currents obtained with the six electrodes were 260, 255, 255, 260, 260, and $250 \mu\text{A}$, respectively, corresponding to a relative standard deviation (RSD) of 1.7%. These results demonstrate excellent electrode-to-electrode reproducibility and confirm the good reliability of the fabrication procedure.

2. Anti-Interference Capability

The complex ionic composition of seawater places stringent requirements on the anti-interference capability of the sensor. Therefore, the influence of common coexisting metal ions on the determination of Pb^{2+} was investigated. A solution containing $100 \mu\text{g/L Pb}^{2+}$ was separately spiked with 150-fold higher concentrations (15 mg/L) of Hg^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , and Cr^{2+} , and the corresponding DPV responses were recorded.

As shown in Figure 7b, the stripping peak current of Pb^{2+} in the absence of interfering ions was approximately $255 \mu\text{A}$. After the addition of Hg^{2+} , Cd^{2+} , Zn^{2+} , Cu^{2+} , and Cr^{2+} , the corresponding peak currents were approximately 260, 250, 260, 265, and $250 \mu\text{A}$, respectively, corresponding to signal variations ranging from -2.0% to 3.9% . These results indicate that the investigated metal ions exerted no significant interference on the determination of Pb^{2+} .

The excellent anti-interference performance can be attributed to several factors. First, within the selected potential window, only Pb^{2+} generated a distinct stripping peak, whereas the stripping potentials of the coexisting metal ions did not overlap with that of Pb^{2+} , thereby minimizing electrochemical signal interference. Second, the abundant amine and imine functional groups of PANI exhibit preferential coordination interactions with Pb^{2+} , resulting in selective recognition of the target ion. Furthermore, the three-dimensional porous architecture of the G-COOH-MWCNTs/PANI composite provides efficient and selective enrichment of Pb^{2+} , further enhancing the selectivity of the sensor.

3. Long-Term Stability

The long-term stability of the sensor was evaluated by monitoring the response of the same modified electrode over a storage period of 35 days. The electrode was stored at 4 °C and tested every seven days using a 100 µg/L Pb²⁺ standard solution under identical experimental conditions.

As shown in Figure 7c, the stripping peak currents recorded on days 1, 7, 14, 21, 28, and 35 were 255, 250, 248, 245, 242, and 240 µA, respectively. After 35 days of storage, the sensor retained 94.1% of its initial response, with an RSD of 2.2%, demonstrating excellent storage stability and indicating its suitability for practical applications.

Overall, these results demonstrate that G-COOH-MWCNTs/PANI/GCE exhibits excellent reproducibility, outstanding anti-interference capability, and good long-term stability, highlighting its considerable potential for the determination of Pb²⁺ in complex seawater matrices.

3.6. Analysis of Real Seawater Samples

To evaluate the practical applicability of the proposed G-COOH-MWCNTs/PANI/GCE electrochemical sensor in complex seawater matrices, seawater samples were collected from the Sanniang Bay coastal area (Dafengjiang Sea Area), Qinzhou, Guangxi, China, and subjected to spike recovery experiments for Pb²⁺ determination.

Immediately after collection, the seawater samples were filtered through a 0.45 µm polytetrafluoroethylene (PTFE) membrane to remove suspended particles, microorganisms, and other potential interferents. The pH of the filtrate was subsequently adjusted to 5.5, and the pretreated samples were stored in sealed containers at 4 °C until analysis.

Prior to measurement, an appropriate volume of the pretreated seawater sample was transferred into the electrochemical cell, followed by the addition of HAc–NaAc buffer (pH 5.5) to obtain a total volume of 10.0 mL. DPV measurements were then performed under the optimized experimental conditions, and the stripping peak current was recorded. The Pb²⁺ concentration in the sample was calculated using the calibration equation ($I_p = 2.757C + 4.316$). To further evaluate the analytical accuracy and reliability of the proposed sensor in real seawater, spike recovery experiments were conducted using the standard addition method. Pb²⁺ standard solutions were added to the seawater samples at three concentration levels (80, 100, and 120 µg/L), and each concentration was measured in triplicate. The recoveries were subsequently calculated, and the results are summarized in Table 5.

Table 5. Recovery results for the determination of Pb²⁺ in real seawater samples (n = 3).

No	Added µg/L	Theoretical µA	Site	Measured µA	Average µA	Measured µg/L	Recovery %	RSD %
1	80	224.88	I	220.32	224.29	79.79	99.73	1.55
			II	225.87				
			III	226.69				
2	100	280.02	I	281.65	276.02	98.55	98.55	2.11
			II	276.39				
			III	270.02				
3	120	335.16	I	330.24	324.34	116.08	96.73	1.59
			II	322.36				
			III	320.41				

As shown in Table 5, the background concentration of Pb²⁺ in the seawater samples was below the detection limit of the proposed method. The recoveries obtained at the three spiking levels ranged from 96.73% to 99.73%, with relative standard deviation (RSD) values below 3.0% (n = 3), demonstrating excellent analytical accuracy and precision in real seawater matrices. Notably, the proposed method requires only simple filtration and pH

adjustment prior to analysis, without complicated sample pretreatment procedures. These results further confirm the excellent anti-interference capability and practical applicability of the G-COOH-MWCNTs/PANI/GCE sensor for the determination of Pb^{2+} in complex seawater environments.

4. Conclusions

In this study, a G-COOH-MWCNTs/PANI composite-based electrochemical sensor was successfully developed for the sensitive determination of Pb^{2+} in seawater. SEM characterization demonstrated that PANI particles were uniformly anchored onto the surfaces of G-COOH-MWCNTs, indicating excellent interfacial compatibility within the composite. Electrochemical characterization revealed that the G-COOH-MWCNTs/PANI-modified electrode exhibited significantly enhanced electrochemical responses toward Pb^{2+} compared with both the bare GCE and the G-COOH-MWCNTs-modified electrode. Furthermore, scan-rate studies confirmed that the electrode process was predominantly diffusion-controlled.

The experimental parameters were systematically optimized through both single-factor experiments and an orthogonal experimental design. The optimum operating conditions were determined to be an HAc–NaAc buffer (pH 5.5), a deposition potential of -1.0 V, a deposition time of 300 s, and a composite film loading of $5\ \mu\text{L}$. The optimal composition of the composite dispersion was found to be $1.0\ \text{mg/mL}$ PANI and $2.0\ \text{mg/mL}$ G-COOH-MWCNTs. Range analysis further demonstrated that the concentration of PANI exerted a greater influence on the sensor response than that of G-COOH-MWCNTs ($R_{\text{PANI}} = 20.8 > R_{\text{G-COOH-MWCNTs}} = 18.1$).

Under the optimized conditions, the proposed sensor exhibited a linear response toward Pb^{2+} over the concentration range of $25\text{--}225\ \mu\text{g/L}$, with the calibration equation $I_p = 2.757C + 4.316$ ($R^2 = 0.997$) and a limit of detection of $0.0337\ \mu\text{g/L}$ ($S/N = 3$). The sensor also demonstrated excellent reproducibility ($\text{RSD} = 1.7\%$), outstanding anti-interference capability (signal variation ranging from -2.0% to 3.9%), and good long-term stability, retaining 94.1% of its initial response after 35 days of storage. Moreover, spike recovery experiments in real seawater samples yielded recoveries ranging from 96.73% to 99.73% , with RSD values below 3% , confirming the excellent analytical accuracy and practical applicability of the proposed sensor for Pb^{2+} determination in seawater.

Overall, the G-COOH-MWCNTs/PANI-based electrochemical sensor provides a simple, sensitive, and reliable analytical platform for the determination of Pb^{2+} in marine environments and shows considerable potential for applications in environmental monitoring and marine pollution assessment.

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