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**Electrochemical Detection of Propyl Gallate in Packaged Foods Using
a SnS₂-Co₁Fe₂@N-CNTs Composite**

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Abstract

Accurate detection of propyl gallate (PG) in packaged foods is crucial for public health. Nevertheless, current electrochemical sensors often rely on noble metals and face a trade-off between sensitivity and fabrication complexity. Herein, we propose a simple interface engineering strategy to construct a noble-metal-free heterostructure of SnS₂ nanoflowers integrated with Co₁Fe₂-layered double hydroxide-decorated nitrogen-doped carbon nanotubes (Co₁Fe₂@N-CNTs). The design capitalizes on the synergistic interplay between SnS₂ and the conductive Co₁Fe₂@N-CNTs scaffold, achieving low charge-transfer resistance and providing abundant accessible catalytic sites. The sensor exhibits a low detection limit of 0.049 μM and a wide linear range of 0.1–1000 μM, surpassing many reported systems without noble metals. The sensor also shows good recoveries (97.68–99.69%) in real food samples, confirming its potential as a reliable and low-cost tool for food safety monitoring. The work provides a strategy for constructing durable sensing interfaces through electronic environment modulation of transition metal compounds, moving beyond conventional material stacking.

Keywords: Propyl Gallate; Co₁Fe₂@N-CNTs; SnS₂; Electrochemical sensor

1. Introduction

Rapid population growth and technological progress have promoted the widespread consumption of processed foods, thereby escalating the use of chemical antioxidants to prolong shelf life [1, 2]. Phenolic antioxidants, particularly propyl gallate (PG), are extensively used as preservatives in food and pharmaceutical products due to their ability to scavenge reactive oxygen species and inhibit oxidative degradation [3, 4]. Beyond food preservation, PG exhibits anti-inflammatory, anticancer, and hepatoprotective effects [5, 6]. However, excessive PG intake poses considerable health risks, including gastrointestinal irritation, hepatorenal toxicity, and potential carcinogenicity [7-9]. Consequently, regulatory authorities in the United States, Australia, China, and other countries have imposed strict limits on PG content in foods [10]. The National Food Safety Standard of China (GB 2760-2011) sets a maximum permitted level of 100 mg/kg for PG in foodstuffs [11]. Therefore, developing reliable methods for the accurate detection and quantification of PG in food and cosmetic products is essential to meet regulatory standards and protect public health.

Several analytical methods have been used to determine PG levels in food and cosmetic samples, such as high-performance liquid chromatography (HPLC), surface-enhanced Raman spectroscopy (SERS), and fluorescence spectroscopy. Although these conventional methods offer high accuracy, they are often time-consuming, rely on costly instrumentation and specialized expertise, and involve complex sample preparation [12]. These constraints limit their practicality for routine and on-site food analysis. Electrochemical sensing offers rapid, sensitive, and selective detection with operational simplicity and low cost [13, 14]. Moreover, its ease of miniaturization and integration into portable systems supports decentralized food safety monitoring. The performance of electrochemical sensors critically depends on electrode surface modification materials [15]. Heteroatom-doped carbon substrates, such as nitrogen-doped carbon (N-C), exhibit outstanding electrocatalytic performance owing to their abundant active sites and excellent electrical conductivity [16, 17]. N-C materials are

generally prepared by pyrolyzing nitrogen-rich precursors at high temperatures, which enhances catalytic activity by modifying charge density within the carbon framework [18]. In this work, nitrogen-doped carbon nanotubes (N-CNTs) were synthesized by pyrolyzing a mixture of melamine and cobalt nitrate, followed by acid leaching to remove the metal catalyst. Nevertheless, these methods often suffer from morphological inconsistency and heterogeneous active sites, limiting catalytic reproducibility.

Layered double hydroxides (LDHs), characterized by a brucite-type architecture of divalent and trivalent metal cations and excellent stability, have been extensively adopted to address these limitations through functionalization of N-C materials [19, 20]. Among various LDHs, Fe/Co-based LDHs have been widely used as promising sensing materials due to their favorable stability and high catalytic activity [21]. However, their poor conductivity and pronounced aggregation tendency severely limit direct electrochemical applications [22, 23]. A widely adopted strategy to address these drawbacks involves immobilizing LDH nanoparticles on conductive carbon substrates, such as graphene and carbon nanotubes [24, 25]. The strategy not only suppresses LDH aggregation but also enhances the catalytic activity of the carbon support, which motivates us to construct a noble-metal-free heterostructure by integrating N-CNTs with CoFe-layered double hydroxide ($\text{Co}_1\text{Fe}_2@\text{N-CNTs}$).

To further enhance the sensing performance, transition metal sulfides (TMSs), such as SnS_2 , were introduced onto the $\text{Co}_1\text{Fe}_2@\text{N-CNTs}$ scaffold. These materials feature layered architectures stabilized by van der Waals forces and are valued for their natural abundance, low toxicity, and eco-friendliness [26, 27]. The introduction of SnS_2 into conductive carbon substrates not only enhances electrical conductivity but also provides supplementary active sites [28, 29]. Specifically, nanoflower-structured SnS_2 provides abundant active sites and surface p-electrons that facilitate strong p- π interactions with N-CNTs, promoting effective interfacial bonding [30-36]. Nevertheless, the application of SnS_2 in PG detection remains underexplored [37, 38].

Recent electrochemical sensors for PG have focused on diverse materials, including noble metal nanoparticles [10], metal oxides [6], and carbon composites [3]. However, these studies have largely adopted a material-stacking approach without addressing the fundamental challenge of achieving high sensitivity, broad dynamic range, and long-term stability in a noble-metal-free platform. The work presents a noble-metal-free $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs}$ heterostructure as an electrochemical platform for PG detection, fabricated via interface engineering to leverage synergistic charge transfer and enhanced catalytic activity. Unlike conventional material-stacking, this strategy deliberately modulates the electronic environment through heterostructure formation, creating a synergistic interface that promotes electron transfer and provides abundant catalytic sites. The resulting sensor achieves a detection limit of $0.049\ \mu\text{M}$ and a linear range of $0.1\text{-}1000\ \mu\text{M}$ for PG, which are competitive with the best reported sensors. In addition, it exhibits excellent reproducibility ($\text{RSD} = 2.8\%$) and robust long-term stability (94.5% retention after 30 days). Compared with previously reported SnS_2 - or LDH-based electrochemical sensors, which typically rely on single-component activity or physical mixtures, our interface-engineered heterostructure offers synergistic catalytic effects arising specifically from the heterointerface between SnS_2 and $\text{Co}_1\text{Fe}_2\text{@N-CNTs}$, combined with the high conductivity of the N-CNT scaffold. These results demonstrate the potential of the $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs}$ heterostructure as a reliable and cost-effective sensing platform for food safety monitoring.

2. Experimental Section

2.1 Reagents and methods

All reagents were of analytical grade and used as received. Melamine ($\text{C}_3\text{H}_6\text{N}_6$), $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, Na_2CO_3 , $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$, thiourea ($\text{CH}_4\text{N}_2\text{S}$), $\text{K}_4[\text{Fe}(\text{CN})_6]$, HNO_3 , ethanol ($\text{C}_2\text{H}_5\text{OH}$), and $\text{K}_3[\text{Fe}(\text{CN})_6]$ were supplied by Aladdin Biochemical Technology Co., Ltd. Na_2HPO_4 and $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ were supplied by China National Pharmaceutical Group Chemical Reagent Co., Ltd.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using a CHI 850D electrochemical workstation (Chenhua Instrument Co., Shanghai, China) in a standard three-electrode configuration. XRD analysis was carried out on a Rigaku Ultima IV diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology and internal microstructure of the synthesized materials were observed via scanning electron microscopy (SEM; ZEISS Sigma 300). X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha) was used to analyze the surface elemental composition, chemical states, and bonding environments of the samples.

2.2 Synthesis of Co₁Fe₂@N-CNTs and SnS₂ Composites

N-CNTs were obtained by grinding melamine and Co(NO₃)₂·6H₂O in ethanol for 30 min. The mixture was vacuum-dried at 50 °C, then pyrolyzed at 1400 °C under N₂ for 2 h. After leaching with HNO₃ to remove cobalt species, the product was rinsed with deionized water until neutral and finally dried to afford N-CNTs.

Fe/Co layered double hydroxide (LDH) nanoflakes were synthesized via coprecipitation. A solution containing FeCl₃·6H₂O (4 mmol) and CoCl₂·6H₂O (2 mmol) was mixed, followed by dropwise addition of Na₂CO₃ (20 mmol) under stirring at 35 °C for 12 h. After washing and drying, the precipitate was ultrasonically mixed with N-CNTs at a 1:2 mass ratio, and the mixture was subsequently dried to obtain Co₁Fe₂@N-CNTs (**Scheme 1**).

SnS₂ was prepared hydrothermally using SnCl₄·5H₂O (0.025 mol) and thiourea (0.15 mol) at 190 °C for 12 h. The SnS₂-Co₁Fe₂@N-CNTs composites were obtained by mixing Co₁Fe₂@N-CNTs with SnS₂ at mass ratios of 1:1, 1:2, and 2:1.

2.3. Preparation of Modified Electrodes

Before electrode modification, a glassy carbon electrode (GCE) was polished with

alumina slurry to remove surface oxides and any scratches, and then rinsed ultrasonically in anhydrous ethanol and deionized water. The $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs}$ catalyst was dispersed in DMF (8 mg/mL) by ultrasonication for 3 h. Then, 4 μL of this dispersion was drop-cast onto the pre-cleaned GCE and air-dried at room temperature before use.

2.4. Real Sample Analysis in Packaged Foods

For real sample analysis, packaged foods (e.g., cured meat, biscuits) were extracted with ethanol and centrifuged (20 min at 5000 rpm). The extraction efficiencies exceeded 90% for both matrices. Matrix effects were evaluated by comparing calibration slopes in buffer and in blank sample extracts (after blank subtraction), with a deviation below 5%, confirming negligible interference. The supernatant was diluted with 0.1 M PBS (pH 7.0) and spiked with PG standards for quantification.

3. Results and discussion

3.1. Preparation and characterization of $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs/GCE}$

A highly sensitive electrochemical sensing platform was constructed by combining $\text{Co}_1\text{Fe}_2\text{@N-CNTs}$ with SnS_2 , aiming to overcome the difficulty of dependable PG quantification at trace levels in complex sample matrices. The sensor was fabricated as illustrated in **Scheme 2**. First, a $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs}$ composite dispersion was drop-coated onto a GCE, yielding a $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs/GCE}$ electrode with high surface area and conductivity. In the structure, $\text{Co}_1\text{Fe}_2\text{@N-CNTs}$ forms a three-dimensional conductive network that provides high electrical conductivity and an electron-rich surface, facilitating rapid electron transfer, while SnS_2 enhances catalytic activity and further improves sensor sensitivity.

Fig. 1 shows representative SEM images of N-CNTs, $\text{Co}_1\text{Fe}_2\text{@N-CNTs}$, and $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs}$. As shown in **Fig. 1a-b**, the N-CNTs form a dense, entangled fibrous network with a heterogeneous diameter distribution. The unaligned CNT morphology

provides active surface area and abundant interfacial contact points, which benefit charge transport and electrolyte infiltration in electrochemical applications. **Fig. 1c-d** show that the $\text{Co}_1\text{Fe}_2@\text{N-CNTs}$ composite consists of LDH flakes aggregated on the N-CNT surface, thereby providing abundant accessible active sites. **Fig. 1e-f** reveal that SnS_2 nanosheets are integrated into and connected with the $\text{Co}_1\text{Fe}_2@\text{N-CNTs}$ framework, indicating the formation of a closely interconnected structure between the two components. These observations indicate that $\text{SnS}_2\text{-Co}_1\text{Fe}_2@\text{N-CNTs}$ is a nanocomposite consisting of intimately integrated SnS_2 , N-CNTs, and Fe/Co LDH components with well-preserved individual morphologies.

The elemental mapping analysis (**Fig. 1g-s**) reveals a uniform distribution of all constituent elements throughout the composite. Quantitative compositional data from EDS analysis are presented in **Fig. 1v**, showing that the composite consists of 87.91% C, 3.82% O, 4.46% Sn, 0.12% N, 0.56% Co, 2.28% S, and 0.85% Fe. These findings confirm successful formation of the $\text{SnS}_2\text{-Co}_1\text{Fe}_2@\text{N-CNTs}$ nanocomposite with the desired elements and uniform spatial distribution.

TEM and HRTEM analyses were performed to investigate the composite microstructure. Low-magnification images (Fig. S1a–b) show SnS_2 nanosheets intimately anchored onto the carbon nanotube network. HRTEM (Fig. S1c) resolves clear lattice fringes of 0.34 nm and 0.31 nm, corresponding to graphitic carbon (002) and SnS_2 (100), respectively, confirming heterointerface formation. Although CoFe LDH fringes were not clearly resolved, likely due to its low crystallinity and loading, XPS and EDS mapping confirm the uniform distribution of Co and Fe species.

XRD was used to determine the crystal phases of the as-prepared samples. As illustrated in **Fig. 2a**, a common diffraction peak appearing around 26° was detected in all samples, which can be assigned to the (002) plane of graphitic carbon [39]. The sharpness and high intensity of this (002) reflection suggest a highly ordered graphitic structure. Distinct diffraction peaks are observed for $\text{Co}_1\text{Fe}_2@\text{N-CNTs}$ at 11.68° , 23.30° , 33.90° , 38.63° , and 46.19° , corresponding to the (003), (006), (012), (015), and

(018) planes, respectively. These peaks are characteristic of a carbonate-intercalated layered double hydroxide and are consistent with JCPDS card No. 50-0235, confirming the successful synthesis of the Co/Fe LDH. Meanwhile, the observed diffraction peaks of the crystalline SnS₂ phase are in good agreement with the standard pattern of pure SnS₂ (JCPDS No. 23-0677). The peaks at specific 2θ values correspond to the (001), (100), (101), (102), (110), (112), (201), and (220) planes of SnS₂ [40, 41]. However, due to their low intensity and partial amorphization upon composite formation, the diffraction peaks of Co/Fe LDH are not observable in the corresponding composites. Thus, XRD confirms successful composite fabrication.

The elemental composition and chemical states of the SnS₂-Co₁Fe₂@N-CNTs composite were characterized by XPS. As shown in the survey spectrum (**Fig. 2b**), characteristic peaks are observed at binding energies of approximately 284.8 eV (C 1s), 400.0 eV (N 1s), 531.0 eV (O 1s), 781.1 eV (Co 2p), 712.8 eV (Fe 2p), 163.5 eV (S 2p), and 486.2 eV (Sn 3d). The C 1s spectrum (**Fig. 2c**) was deconvoluted into four peaks located at 284.36, 284.80, 286.23, and 288.20 eV, corresponding to C=C, C-C, C-O/C-N, and O=C-C functionalities, respectively. These findings confirm the coexistence of sp²- and sp³-hybridized carbon species along with oxygen-containing groups [41, 42]. The O 1s spectrum (**Fig. 2d**) was deconvoluted into three peaks at 531.42, 532.84, and 533.93 eV, corresponding to O=C, HO-C, and O=C-OH bonds, respectively. These assignments indicate the presence of various oxygen coordination environments within the material. As shown in **Fig. 2e**, the N 1s spectrum can be resolved into four distinct species: pyridinic N (398.41 eV), pyrrolic N (399.90 eV), graphitic N (401.02 eV), and oxidized N (N-O, 403.50 eV) [43, 44]. The finding demonstrates that nitrogen dopants are incorporated into the carbon framework in multiple chemical configurations. The Co 2p_{3/2} spectrum (**Fig. 2f**) shows peaks at 780.95 eV (Co³⁺) and 782.03 eV (Co²⁺), with shake-up satellites at 785.78 eV. Deconvolution of the Co 2p spectrum confirms the coexistence of Co²⁺ and Co³⁺ in the composite. The partial oxidation of Co²⁺ to Co³⁺ during synthesis introduces high-valence cobalt species, which act as efficient active sites for oxidation reactions. The finding indicates that the SnS₂-Co₁Fe₂@N-CNTs

composite exhibits enhanced oxidation activity. The Fe 2p spectrum (**Fig. 2g**) reveals that iron retains the +3 oxidation state in the composite, consistent with that of bare Fe/Co LDH. The Fe 2p_{3/2} peak at 711.20 eV, together with the spin–orbit splitting (typical for Fe³⁺), confirms this assignment, whereas Fe²⁺ would exhibit a distinctly lower binding energy. The S 2p spectrum of the SnS₂-Co₁Fe₂@N-CNTs composite (**Fig. 2h**) shows two distinct signals at 162.06 eV and 160.83 eV, which are assigned to the S 2p_{1/2} and S 2p_{3/2} levels, respectively, suggesting that sulfur exists in the S²⁻ oxidation state. The Sn 3d XPS spectrum (**Fig. 2i**) exhibits two well-resolved peaks at 485.86 eV and 494.30 eV, corresponding to the Sn 3d_{5/2} and Sn 3d_{3/2} doublets, consistent with Sn⁴⁺ in SnS₂. A slight low-binding-energy asymmetry may indicate trace surface defects or partial reduction, although the signal-to-noise ratio does not permit reliable quantification. Sn⁴⁺ is unequivocally the dominant species, confirming the formation of SnS₂.

N₂ physisorption (Fig. S2a–b, Table S1) reveals BET surface areas of 75.89 and 77.99 m² g⁻¹ for N-CNTs and Co₁Fe₂@N-CNTs, respectively, which decrease to 59.30 m² g⁻¹ upon SnS₂ integration due to pore coverage. All three samples exhibit type IV isotherms with H3-type hysteresis loops (Fig. S2a) and mesoporous pore size distributions (Fig. S2b), with average pore sizes of 8.36, 6.36, and 6.21 nm, respectively. Notably, despite the modest BET reduction, the composite retains its mesoporous structure while exhibiting a substantially enlarged ECSA (0.230 cm², Table S2) compared with N-CNTs (0.111 cm²) and Co₁Fe₂@N-CNTs (0.161 cm²). The combination ensures sufficient active site exposure, effectively offsetting the BET decrease and underpinning the enhanced sensing performance.

3.2 Electrochemical characterization of SnS₂-Co₁Fe₂@N-CNTs

As shown in **Fig. 3a**, the SnS₂-Co₁Fe₂@N-CNTs/GCE delivers the highest redox peak current, substantially surpassing the background signal. This pronounced improvement demonstrates that the synergistic integration of SnS₂ with Co₁Fe₂@N-

CNTs accelerates the electron-transfer kinetics and enlarges the electrochemically active surface area. In agreement with the CV results, a substantially higher DPV response compared to the background is also observed for the SnS₂-Co₁Fe₂@N-CNTs/GCE (**Fig. S3**). Electrochemical impedance spectroscopy (EIS) was employed to probe the interfacial properties of each modified electrode (**Fig. 3b**). The Nyquist plots were fitted using a Randles-type equivalent circuit composed of solution resistance (R_s), constant phase element (CPE, representing double-layer capacitance), charge-transfer resistance (R_{ct}), and Warburg impedance (W) [45]. A baseline R_{ct} of 621.5 Ω is observed for the unmodified GCE. Following modification with SnS₂, N-CNTs, and Co₁Fe₂@N-CNTs, the R_{ct} values decrease to 212.1, 146.3, and 98.7 Ω , respectively, indicating that all three modifications facilitate charge transfer, with the latter two showing more pronounced enhancement. In contrast, the SnS₂-Co₁Fe₂@N-CNTs/GCE delivers a substantially lower R_{ct} of 26.8 Ω , reflecting markedly enhanced electron transfer kinetics and superior conductivity. The marked reduction in R_{ct} is attributed to the cooperative coupling between SnS₂ and the Co₁Fe₂@N-CNTs framework. The synergistic interaction not only increases the electroactive surface area but also promotes efficient ion diffusion and electron migration. Consequently, the proposed sensor exhibits superior charge transfer efficiency compared to many previously reported electrochemical platforms for antioxidant detection.

To optimize the composite composition, three mass ratios of Co₁Fe₂@N-CNTs to SnS₂ (1:1, 1:2, and 2:1) were investigated. As shown in **Fig. 3c-d**, the 1:1 ratio produced the highest current response, indicating optimal synergistic interaction between the two components. An excess of either Co₁Fe₂@N-CNTs or SnS₂ caused agglomeration, which reduced active site exposure and electrical conductivity. Structural characterization of the three mass-ratio samples was not performed, as the primary focus of this work was on optimizing the electrochemical sensing performance. Nevertheless, the reliability of the optimization was ensured by consistent electrochemical trends across multiple batches ($n=3$), with the 1:1 ratio consistently yielding the highest DPV current response. Therefore, the 1:1 ratio provided the best

balance between active site accessibility and charge transport efficiency. The effect of scan rate on the electrochemical response of the SnS₂-Co₁Fe₂@N-CNTs/GCE was investigated by CV in the same redox probe system. As the scan rate rose from 10 to 100 mV·s⁻¹ (**Fig. 3e**), the peak currents increased progressively. The peak current showed a linear dependence on the square root of the scan rate (**Fig. 3f**), revealing that the electrode process is governed by diffusion control – a desirable characteristic for achieving dependable electrochemical sensing.

The ECSA of the SnS₂-Co₁Fe₂@N-CNTs/GCE was calculated using the Randles-Ševčík equation to be 0.230 cm² (Table S2), substantially larger than those of bare GCE (0.0829 cm²), SnS₂/GCE (0.0997 cm²), N-CNTs/GCE (0.111 cm²), and Co₁Fe₂@N-CNTs/GCE (0.161 cm²). This confirms the superior charge-transfer kinetics and abundant accessible active sites of the composite. Taken together, the electrochemical characterization results indicate that the SnS₂-Co₁Fe₂@N-CNTs composite serves as a high-performance sensing platform, offering accelerated electron transfer kinetics, a substantial electroactive surface area, and a well-optimized compositional balance. These attributes render it highly promising for the sensitive monitoring of PG. Although the XPS data do not allow reliable quantification of defect species, the increased ECSA and reduced R_{ct} observed at the composite electrode are consistent with beneficial surface defects on SnS₂, which may serve as adsorption sites for PG and facilitate charge transfer, synergistically with the conductive Co₁Fe₂@N-CNTs network.

3.3 Electrochemical behavior of SnS₂-Co₁Fe₂@N-CNTs towards PG

Cyclic voltammetry (CV) of bare GCE, SnS₂/GCE, N-CNTs/GCE, Co₁Fe₂@N-CNTs/GCE, and SnS₂-Co₁Fe₂@N-CNTs/GCE was carried out in 0.1 M PBS (pH 7.0) containing 1 mM PG between -0.2 and 0.6 V (**Fig. 4a**). Clear oxidation peaks associated with PG were observed for all electrodes (**Fig. 4a–b**). The bare GCE gave an I_{pa} of only 4.95 μA, suggesting poor electron transfer kinetics. Upon modification with N-

CNTs, the anodic current increased to 9.49 μA , and further rises were recorded for SnS₂/GCE (24.25 μA) and Co₁Fe₂@N-CNTs/GCE (25.86 μA). Most importantly, the SnS₂-Co₁Fe₂@N-CNTs/GCE composite exhibited the maximum peak current (54.14 μA), demonstrating a robust synergistic interplay between its components. Compared with single-metal LDH, the binary LDH exhibits superior redox activity, and the SnS₂-Co₁Fe₂@N-CNTs/GCE composite supported on the bare electrode provides higher catalytic activity. These results confirm that the enhanced performance arises from synergistic coupling rather than from the intrinsic activity of either component alone. The resulting heterojunction facilitates rapid electron transfer and offers abundant active sites, thereby substantially enhancing interfacial interactions. Consequently, this composite serves as an excellent candidate for the electrochemical detection of PG.

Furthermore, optimization of the modifier loading (**Fig. 4c**) revealed that a 4 μL aliquot of the SnS₂-Co₁Fe₂@N-CNTs dispersion produced the highest current response. Lower loadings resulted in insufficient active sites, whereas excessive loadings hindered electron transfer due to increased layer thickness and diffusion resistance. Using DPV, the pH dependence of the PG electrochemical signal at the modified electrode was examined across a pH window of 3.0-11.0. As illustrated in **Fig. 4d**, raising the pH from 3.0 to 7.0 led to an increase in the anodic peak current, which peaked at pH 7.0 and then progressively declined under alkaline conditions. The observed pattern suggests that neutral conditions promote the electrooxidation of PG, which can be explained by a favorable equilibrium between the supply of protons and the persistence of electroactive species. The decrease at higher pH is attributed to the deprotonation of PG, which reduces its affinity for the electrode surface. Hence, a pH value of 7.0 was chosen for the PBS used in all later experiments. Collectively, these findings confirm that the SnS₂-Co₁Fe₂@N-CNTs composite provides superior catalytic performance alongside efficient charge transfer, positioning it as a highly suitable platform for PG electroanalysis.

The reaction kinetics were studied via CV using scan rates of 10–100 mV/s in a solution containing 1 mM PG (**Fig. 4e**). **Fig. 4f** illustrates a linear relationship between the anodic peak current (I_{pa}) and the square root of the scan rate ($v^{1/2}$), as described by the following equation:

$$I_{pa} (\mu A) = 10.75 v^{1/2} + 9.15 (R^2=0.998) \quad (1)$$

The linear dependence of the anodic peak current (I_{pa}) on the square root of scan rate ($v^{1/2}$), with a near-zero intercept ($R^2 = 0.998$), indicates a diffusion-controlled process, as opposed to an adsorption-controlled one which would exhibit a linear I_{pa} - v relationship. This behavior is consistent with the Randles–Sevcik equation and is advantageous for quantitative analysis, as it ensures a stable and predictable current–concentration correlation over a wide linear range. To gain insight into the electron transfer kinetics, the correlation between E_{pa} and $\ln v$ (where v is the scan rate) was studied (**Fig. S4**). The positive shift of E_{pa} with increasing scan rate indicates an irreversible oxidation process, consistent with the typical behavior of phenolic compounds.

The charge-transfer coefficient (α) was experimentally determined from the Tafel slope ($b = 119 \text{ mV dec}^{-1}$), giving $\alpha = 0.49$, which closely matches the assumed value of 0.5. Using this α value in Laviron’s equation for an irreversible process, the electron number (n) for the rate-limiting step was calculated to be approximately 2. Additionally, the anodic peak potential (E_{pa}) shifted linearly with pH with a slope close to the Nernstian value of -59 mV pH^{-1} (**Fig. S5**), indicating equal proton and electron participation. These results confirm that PG electrooxidation proceeds via a $2H^+/2e^-$ coupled mechanism. The result suggests that the oxidation of PG at the modified electrode proceeds via a two-electron, two-proton process. The finding aligns with the oxidation mechanism proposed for gallate derivatives.

Fig. 5a shows the DPV curves recorded at the modified electrode upon sequential addition of PG over concentrations spanning from 0.1 to 1000 μM . A gradual increase

in PG concentration led to a corresponding rise in the anodic peak current, indicating a sensitive and concentration-proportional electrochemical behavior. The calibration plot (**Fig. 5b**) reveals a highly linear correlation between the peak current (I_p) and PG concentration over the whole concentration interval examined. The resulting linear regression equation is $I_p (\mu A) = 133.7944 C (mM) + 1.0428$, yielding a correlation coefficient (R^2) of 0.997, which reflects excellent linearity of the sensor response. The limit of detection (LOD) was determined as 0.049 μM within the linear range of 0.1–1000 μM , according to the following formula:

$$LOD = 3\sigma/k \quad (2)$$

Where σ is the standard deviation of 12 independent blank measurements in PBS (2.185 $\times 10^{-3}$ μA) and k is the slope of the calibration curve. The calibration curve was constructed with 14 concentration points, each measured in triplicate. The obtained LOD of 0.049 μM is substantially lower than the maximum residue limits established by food safety regulations, confirming the suitability of the proposed sensor for routine trace-level monitoring.

To assess the selectivity of the $SnS_2-Co_1Fe_2@N-CNTs/GCE$, its DPV signal for PG was recorded after introducing various potential interferents, namely tetracycline (TC), copper(II) sulfate ($CuSO_4$), caffeic acid (CF), succinimidyl carbonate (SC), sodium sulfite (Na_2SO_3), glucose (Glc), uric acid (UA), Coomassie brilliant blue (CBB), sodium nitrate ($NaNO_3$), eugenol (EG), Potassium nitrate (KNO_3), calcium chloride ($CaCl_2$), sodium phosphate (Na_3PO_4), and ascorbic acid (AA). **Fig. 5c and 5d** demonstrate that adding a 100-fold molar excess of interfering substances caused only minor fluctuations in the peak current (relative deviation < 8%). Although TC, CF, and EG contain phenolic moieties, their electrooxidation occurs at distinctly different potentials from PG due to differences in their substituent groups, as reflected by the absence of observable current responses at the PG oxidation potential in the DPV measurements.

The outstanding selectivity stems from the synergistic interplay of SnS_2 and

Co₁Fe₂@N-CNTs, which facilitates selective PG recognition through favorable molecular interactions while suppressing non-specific adsorption of interfering species.

The reproducibility and repeatability of the proposed sensor were further evaluated. As shown in **Fig. 5e**, the DPV signals obtained from seven individually prepared electrodes in the presence of 0.1 mM PG were highly consistent, with a relative standard deviation (RSD) of 2.8%, reflecting excellent reproducibility of the fabrication process. In addition, the intra-electrode repeatability was examined by performing twelve successive measurements under identical conditions, giving an RSD of 3.2% (**Fig. 5f**). In addition, the batch-to-batch reproducibility was assessed using two independently prepared electrodes (**Fig. S6 and S7**), with an RSD of less than 5% (n=3). These findings attest to the robustness and dependability of the SnS₂-Co₁Fe₂@N-CNTs-based sensing platform. For practical sensing applications, long-term operational stability also represents a key factor. The long-term storage stability of the SnS₂-Co₁Fe₂@N-CNTs/GCE was evaluated by DPV for 100 μM PG after 30 days storage at room temperature (**Fig. 5g**). The sensor retained 94.5% of its initial current. To verify structural stability during electrochemical operation, post-mortem XRD analysis was performed on the electrode material after 50 CV cycles (**Fig. S8**). The used electrode exhibits expected peak broadening due to cycling-induced amorphization, but no impurity peaks from detached phases appear, and the characteristic signals of SnS₂ and Co₁Fe₂ LDH are preserved. These results confirm that no macroscopic component separation occurs during electrochemical testing, demonstrating the structural robustness of the nanocomposite.

To further validate the practical utility of the SnS₂-Co₁Fe₂@N-CNTs/GCE, its analytical reliability was assessed through recovery experiments in real food matrices. As presented in **Table S3**, the ability of the sensor to detect PG was tested on biscuit and cured meat samples spiked with predetermined concentrations. Recovery values varied between 97.68% and 99.69%, and the corresponding RSDs remained under 2.6% (n = 3), which attests to the method's high accuracy and precision. Collectively, these data affirm that the proposed sensor can reliably quantify PG in complicated food

substrates, with no notable matrix effects. The reliability of the SnS₂-Co₁Fe₂@N-CNTs/GCE for PG quantification was further confirmed by analyzing the same real samples (biscuits and cured meat) using a validated HPLC method. As shown in **Fig. 5h**, the overlaid HPLC chromatograms at different PG concentrations (0, 50, 100, 200, and 300 μ M) exhibit well-resolved peaks whose retention times are consistent with the PG standard. The corresponding calibration curve (**Fig. 5i**) exhibits excellent linearity ($R^2 = 0.999$), confirming the suitability of the HPLC method as a reference.

The results obtained by the proposed SnS₂-Co₁Fe₂@N-CNTs electrochemical sensor (**Table S3**) and the HPLC method (**Table S4**) show good agreement, with only minor deviations. The two methods exhibited a maximum relative difference of approximately 3.2%, with all recovery values ranging from 95.52% to 100.28%, which falls within the acceptable range. These minor discrepancies are expected when comparing a new electrochemical sensor with a reference chromatographic method. The electrochemical sensor is based on direct PG oxidation at the modified electrode surface, while HPLC requires separation, elution, and UV detection. Minor differences arising from selectivity and matrix effects are unavoidable. However, these deviations are not statistically significant, as indicated by the overlapping RSD values ($n = 3$) and the consistently high recoveries. Thus, the HPLC-based verification attests to the accuracy and dependability of the developed SnS₂-Co₁Fe₂@N-CNTs sensing platform for quantifying PG in real food matrices. As illustrated in **Fig. 5**, the nanocomposite displays a broad linear calibration range (0.1-1000 μ M), an extremely low limit of detection (0.049 μ M), superior selectivity, and outstanding stability. These characteristics demonstrate the sensor's potential for practical food safety monitoring, particularly for on-site detection of PG residues in packaged foods.

The analytical performance of the SnS₂-Co₁Fe₂@N-CNTs/GCE was compared with recently reported modified electrodes for PG detection (**Table S5**). While several existing sensors achieve low detection limits, our noble-metal-free platform offers a balanced combination of a wide linear range (0.1-1000 μ M), a low LOD (0.049 μ M), and excellent reproducibility. Its facile synthesis and stable signal further support its

practicality for routine food analysis. Moreover, the heterostructure design may be extended to other gallate-type antioxidants, and integration into portable devices could enable on-site food safety surveillance.

4. Conclusion

In summary, a noble-metal-free electrochemical platform for PG detection has been successfully developed based on a $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs}$ heterostructure. The rational integration of SnS_2 with $\text{Co}_1\text{Fe}_2\text{-LDH}$ on a N-CNTs support generates a synergistic interface that markedly accelerates charge-transfer kinetics and affords abundant catalytic sites. As a result, the developed sensor exhibits excellent performance for PG detection, achieving a detection limit of $0.049\ \mu\text{M}$, a linear range of $0.1\text{-}1000\ \mu\text{M}$, and good reproducibility ($\text{RSD} = 2.8\%$), with recoveries of $97.68\text{-}99.69\%$ in real food samples. Moreover, this work provides a generalizable strategy for designing noble-metal-free sensing interfaces via heterostructure engineering, which is potentially extendable to other antioxidants and electroactive contaminants.

Declarations

Conflict of Interest

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

Ethical Approval

This research did not involve human or animal samples.

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AI Disclosure

During the preparation of this manuscript, the author(s) used DeepSeek to polish and improve the language of the text. The tool was used solely for language editing and did not contribute to the generation of scientific content, data analysis, interpretation of results, or the preparation of figures and graphical abstracts. The author(s) reviewed and edited all AI-assisted text and take full responsibility for the content of the final manuscript. The figures and graphical abstract in this manuscript were created by the author(s) without the use of Artificial Intelligence (AI) tools.

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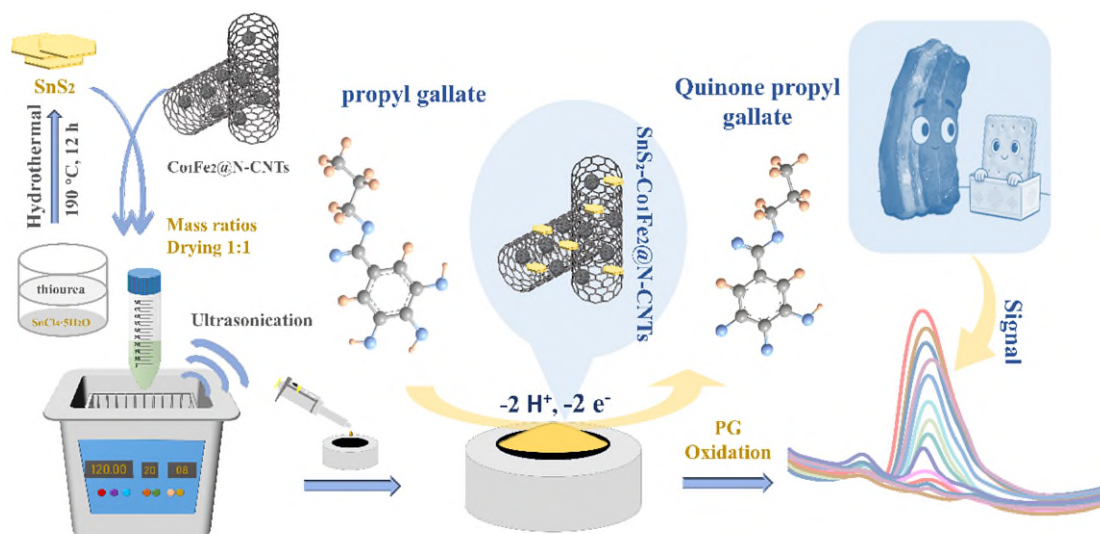
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Graphic abstract



A highly sensitive electrochemical sensing platform was constructed by combining $\text{Co}_1\text{Fe}_2\text{@N-CNTs}$ with SnS_2 to enable dependable trace-level quantification of propyl gallate (PG) in complex food matrices. The sensor exhibits a wide linear range (0.1–1000 μM) and a low detection limit of 0.049 μM , with high recovery rates, good stability, and robust anti-interference performance in real commercial packaged food samples. The enhanced catalytic activity arises from the synergistic interplay between SnS_2 and $\text{Co}_1\text{Fe}_2\text{@N-CNTs}$, which increases active site availability.

Electrochemical Detection of Propyl Gallate in Packaged Foods Using a $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs}$ Composite

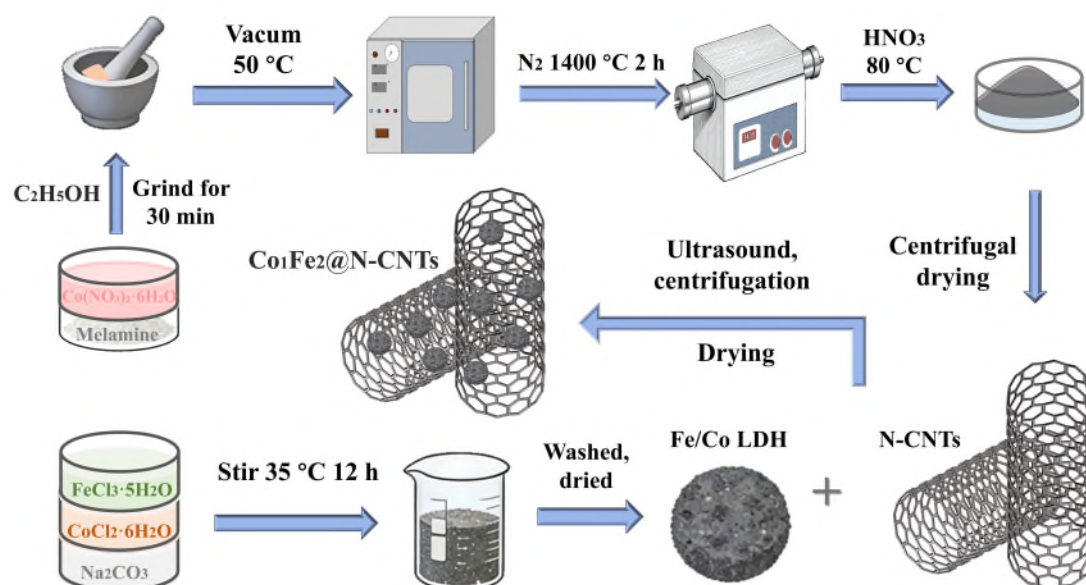
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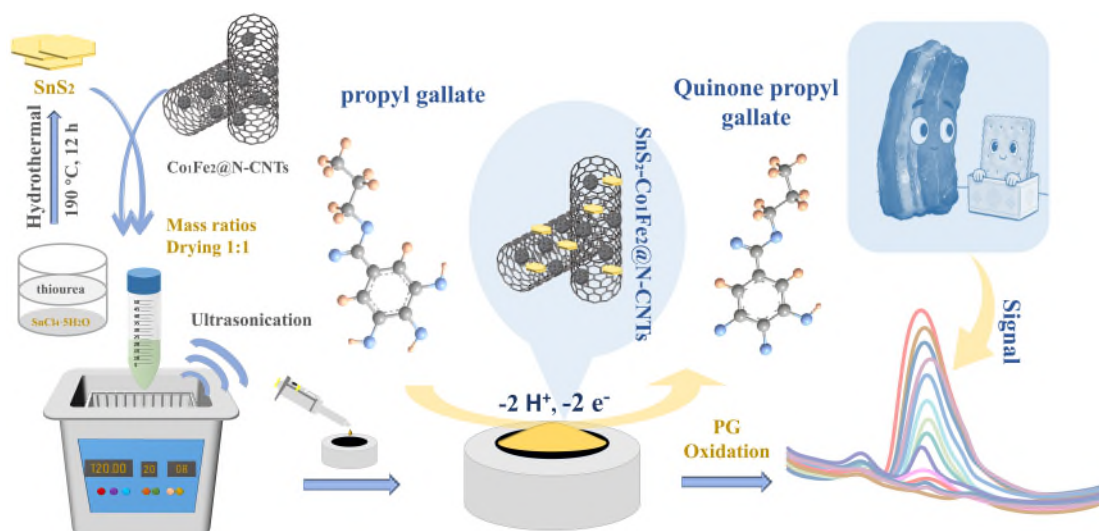
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Scheme 1. Schematic illustration of the synthetic routes for N-CNTs, Fe/Co LDH, and the $\text{Co}_1\text{Fe}_2\text{@N-CNTs}$ composite.



Scheme 2. Schematic representation of PG determination in food samples using the $\text{SnS}_2\text{-Co}_1\text{Fe}_2\text{@N-CNTs}$ composite.

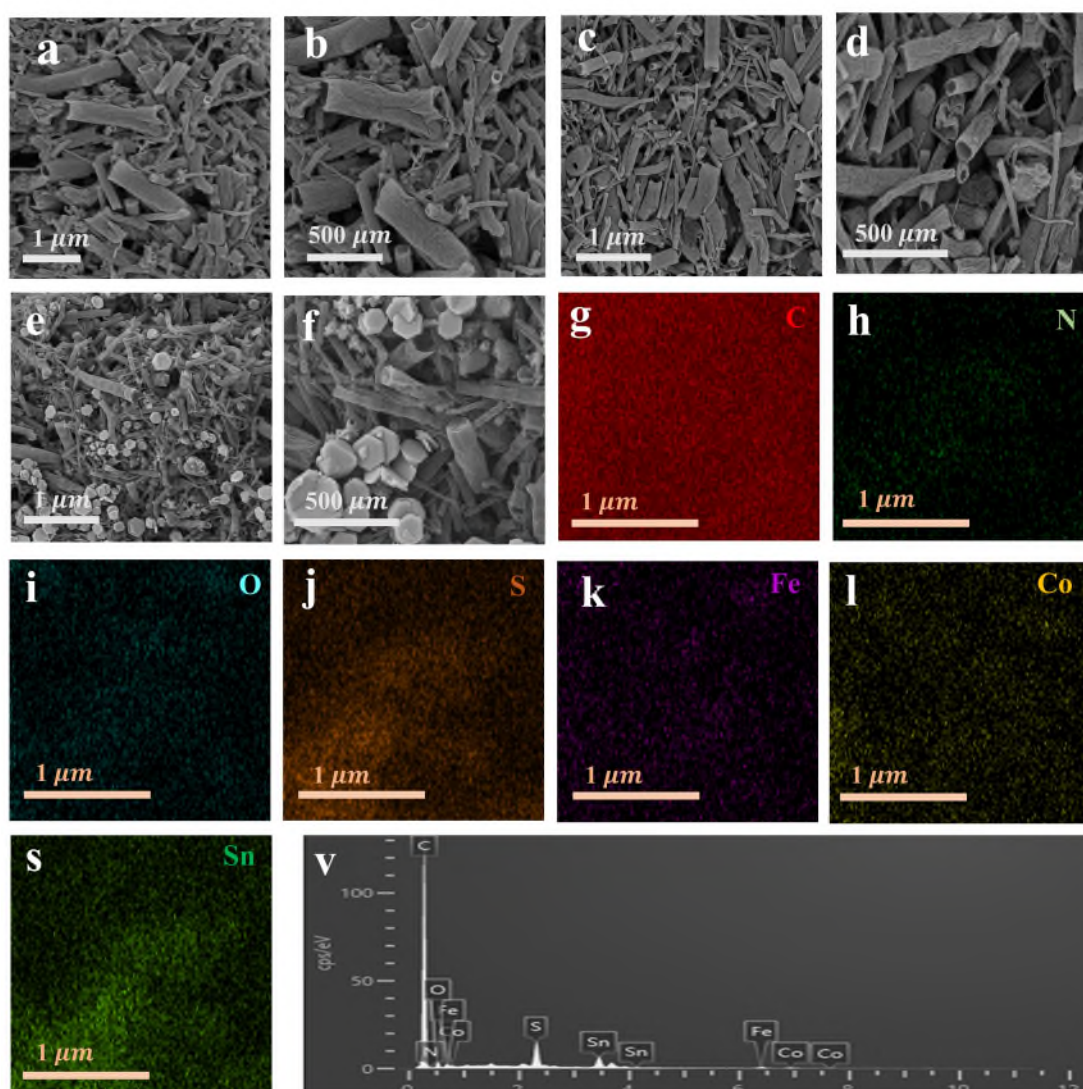


Fig. 1a-f SEM analysis of nanomaterials. (a-b) Magnified image of N-CNTs, (c-d) $\text{Co}_1\text{Fe}_2@\text{N-CNTs}$ (e-f) $\text{SnS}_2\text{-Co}_1\text{Fe}_2@\text{N-CNTs}$ and (g-v) EDS spectra of $\text{SnS}_2\text{-Co}_1\text{Fe}_2@\text{N-CNTs}$ nanostructures.

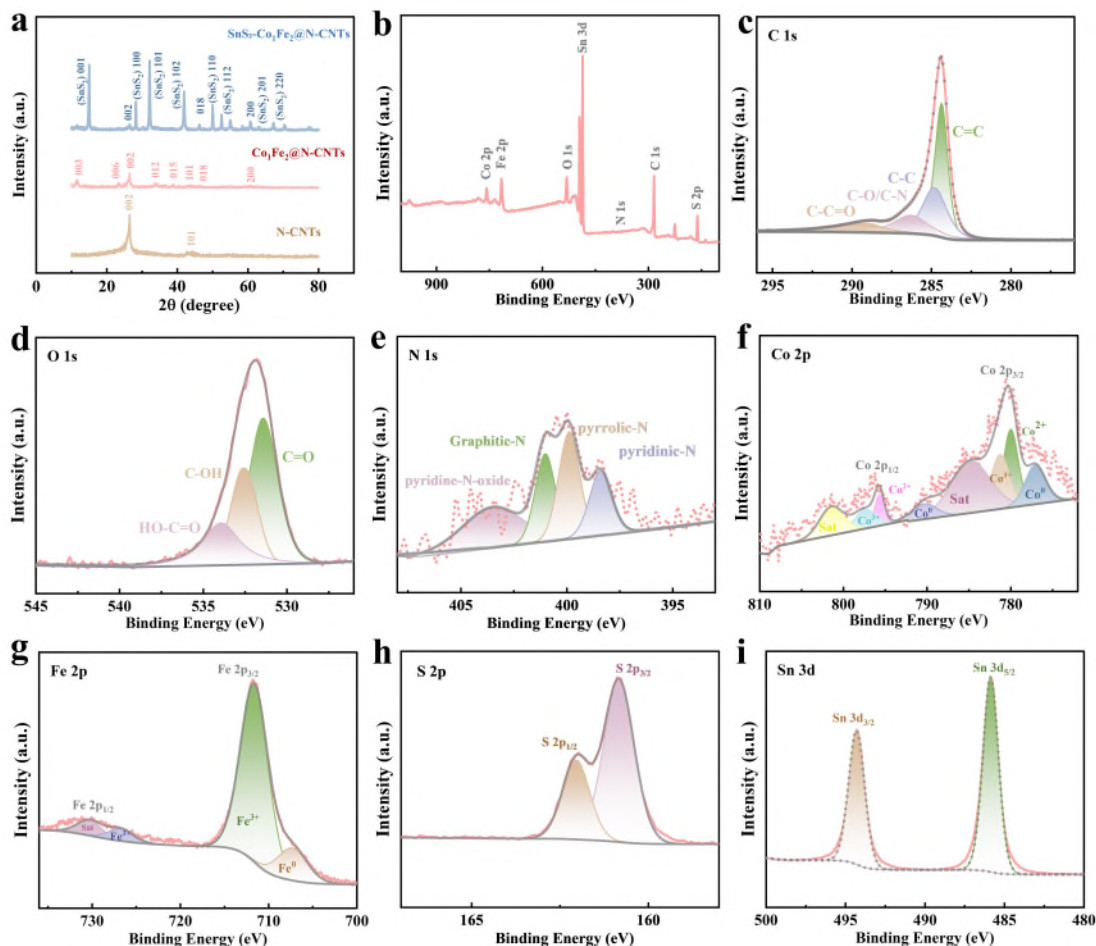


Fig. 2. (a) XRD patterns recorded for N-CNTs, $\text{Co}_1\text{Fe}_2@\text{N-CNTs}$, and the $\text{SnS}_2\text{-Co}_1\text{Fe}_2@\text{N-CNTs}$ composite. (b) XPS survey spectrum of the $\text{SnS}_2\text{-Co}_1\text{Fe}_2@\text{N-CNTs}$ composite. (c-i) High-resolution XPS spectra of C 1s, O 1s, N 1s, Co 2p, Fe 2p, S 2p, and Sn 3d, respectively.

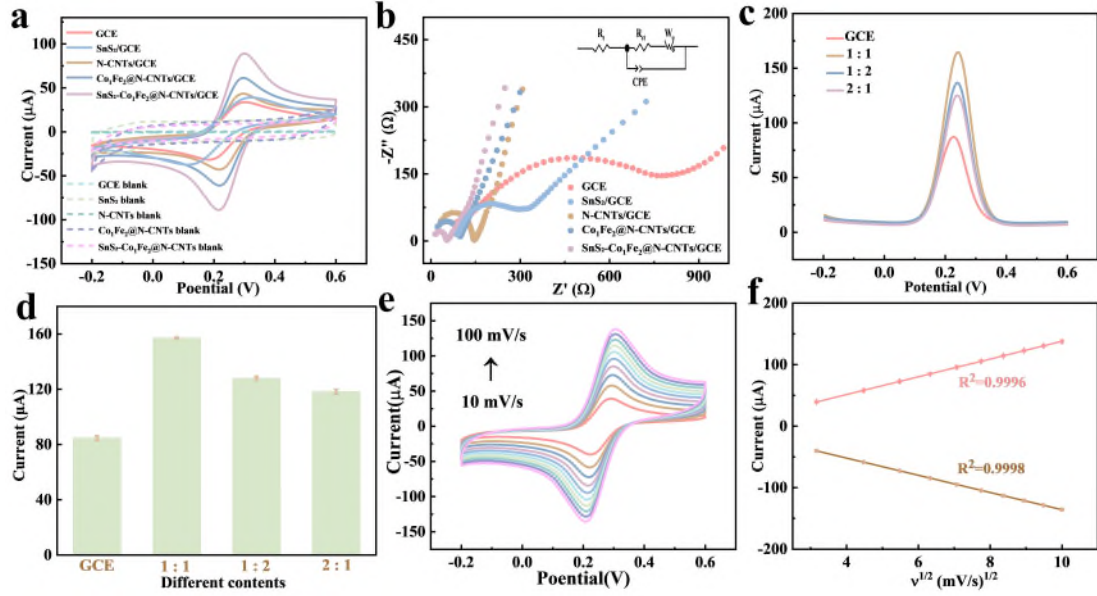


Fig. 3. (a) CV curves measured in 2.5 mM Fe(CN)₆^{3-/4-}; (b) EIS signals under the same electrolyte conditions; (c) DPV patterns for electrodes with distinct component mass ratios; (d) bar chart illustrating peak current variations; (e) CV curves of SnS₂-Co₁Fe₂@N-CNTs recorded at scan rates of 10–100 mV·s⁻¹; (f) plot of peak current vs. square root of scan rate with linear regression.

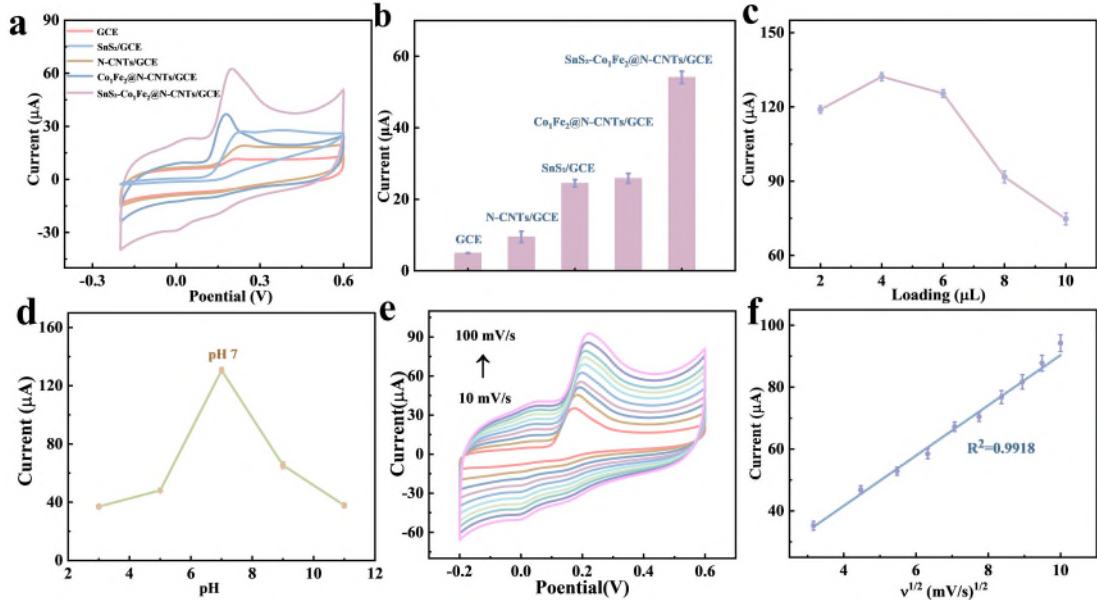


Fig. 4. (a) Cyclic voltammetry responses of the SnS₂-Co₁Fe₂@N-CNTs/GCE measured in 0.1 M PBS containing 1 mM PG at a scan rate of 50 mV·s⁻¹; (b) histogram showing

the corresponding anodic peak currents; (c) effect of the modifier loading (volume of SnS₂-Co₁Fe₂@N-CNTs dispersion) at pH 7 on the sensor response; (d) pH dependence of the PG sensor based on SnS₂-Co₁Fe₂@N-CNTs/GCE; (e) CV curves of the SnS₂-Co₁Fe₂@N-CNTs/GCE obtained over a scan rate range of 10–100 mV·s⁻¹; (f) linear fit showing the dependence of the anodic peak current on the square root of the scan rate ($v^{1/2}$).

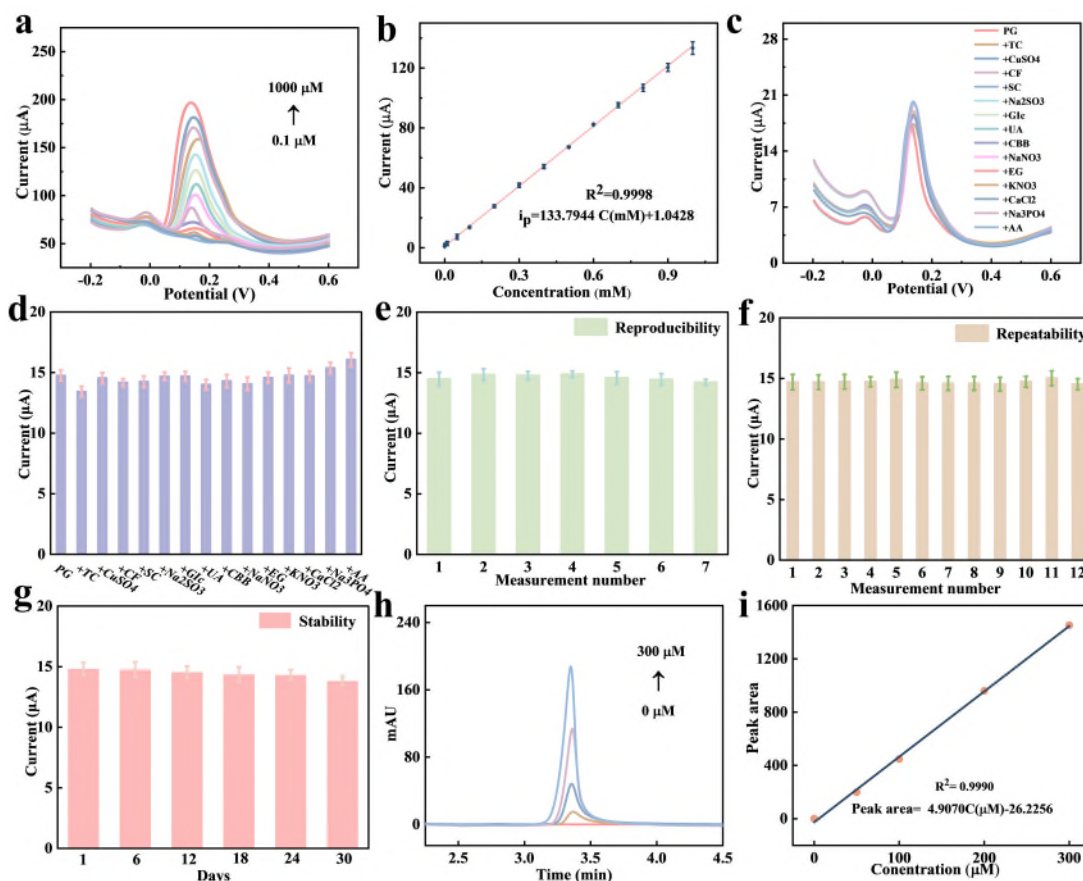


Fig. 5. (a) DPV responses of the SnS₂-Co₁Fe₂@N-CNTs/GCE to successive additions of PG in the concentration range of 0.1 to 1000 μM; (b) corresponding calibration plot of PG concentration versus anodic peak current (I_p); (c) DPV curves recorded in the presence of 0.1 mM PG with various interfering analytes; (d) histogram of the average current responses for the interfering species; (e) reproducibility; (f) repeatability; (g) long-term stability; (h) overlaid HPLC chromatograms of PG samples at indicated concentrations; (i) linear calibration curve of absorbance versus PG concentration.

Supplementary Files

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