

Hydrothermally Synthesized SnO₂/Reduced Graphene Oxide Nanocomposite as a Solid-Contact Layer for Potentiometric Nitrate Sensing

Percy Sephra

B.S. Abdur Rahman Crescent Institute of Science & Technology

Tharini Chandrapragasam

tharini@crescent.education

B.S. Abdur Rahman Crescent Institute of Science & Technology

Research Article

Keywords: Hydrothermal method; Open circuit potential, Ion selective membrane, cyclic voltammetry, nitrate sensing

Posted Date: October 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11096105/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Hydrothermally Synthesized SnO₂/Reduced Graphene Oxide Nanocomposite as a Solid-Contact Layer for Potentiometric Nitrate Sensing

¹Percy J.Sephra, ² Tharini Chandrapragasam*

^{1,2} Centre for Sensors and System Design, Department of Electronics and Communication Engineering, B.S.Abdur Rahman Crescent Institute of Science & Technology, Chennai 600048, India

Corresponding email: tharini@crescent.education

Abstract

A CTAB-assisted hydrothermal method was employed to synthesize SnO₂ and SnO₂/rGO nanocomposites, which were subsequently characterized to evaluate their structural, morphological, and physicochemical properties. These nanomaterials were then integrated with ion-selective membranes (ISM) to assess their potentiometric performance for nitrate sensing. X-ray diffraction (XRD) analysis confirmed the crystalline tetragonal rutile phase of SnO₂, with a preferential (211) orientation. Incorporation of rGO preserved SnO₂ crystallinity while enhancing interfacial interactions, as evidenced by intensified (110) diffraction and characteristic rGO peaks. Complementary FTIR, Raman, and microscopic analyses validated successful composite formation. Electrochemical studies carried out using cyclic voltammetry in phosphate-buffered solution (PBS) revealed that rGO incorporation significantly enhanced charge storage and redox behavior due to improved conductivity and surface area. Potentiometric performance was assessed through open-circuit potential (OCP) measurements upon successive additions of nitrate (NO₃⁻) ions. The ISM–SnO₂ electrode demonstrated a sensitivity of 0.04703 ± 0.00197 V/decade over a concentration range of 1–120 ppm ($R^2 = 0.9879$), while the ISM–SnO₂/rGO electrode achieved a higher sensitivity of 0.06379 ± 0.00486 V/decade and an extended detection range up to 240 ppm ($R^2 = 0.9718$). This enhancement is attributed to the synergistic effect of rGO, which facilitates efficient ion-to-electron transduction and accelerates nitrate reduction. The TDAN-based ISM enabled selective nitrate extraction via electrostatic and hydrogen-bond interactions, followed by electrochemical reduction at the rGO-enhanced SnO₂ interface. These findings highlight the ISM-SnO₂/rGO platform as a promising candidate for sensitive and selective electrochemical nitrate detection in environmental and biomedical applications.

Keywords: Hydrothermal method; Open circuit potential, Ion selective membrane, cyclic voltammetry, nitrate sensing.

Introduction

Contamination of surface and groundwater due to excessive use of fertilizer has caused major environmental pollution and led the research community towards technology that aims to rapidly, high-throughput, and on-site detection of contaminants present in the soil. In agriculture, nitrate is the primary fertilizer, excessive usage of which leaches easily from the soil, causing eutrophication, increasing toxicity[1][2][3]. Hence, developing technology enabling regular, adequate monitoring with simple, low cost is of continuing interest. Monitoring nitrate fertilizer is of importance, as insufficient NO_3^- fertilizer reduces crop production and excessive usage affects the environment[4]. Several laboratory-based measurement techniques, like ultraviolet visible (UV) spectrophotometry, gas chromatography, and chemiluminescence, are available[5]. Although these methods exhibit superior performance by providing high sensitivity and selectivity, they need laborious, increased complexity, and time-consuming tasks, which limit practical operation in fields.

As a result, various solid-state sensors have been developed to detect NO_3^- . Ion-selective electrodes (ISEs) are commonly used, cost-effective electrochemical sensors for detecting specific analytes of interest based on potential measurements[6]. ISEs are advantageous and good for commercial use due to their compact size, high selectivity, and ability to integrate with portable devices for on-site monitoring of the analyte of interest. Applications of ISE include a wide range from agriculture, medical diagnostics, and environmental applications. ISEs are developed by coating a thin metal wire with the ion-selective membrane (ISM), but a capacitive interface is created with the wire, as the redox-active charged species are difficult to transfer to the wires. Metal wire-based ISE was developed in 1971; these don't require an internal filling solution as needed in conventional ISEs, but it has weak potential response and poor stability due to the lack of redox species[7]. Conventional ISE requires an inner filling solution between the inner reference (non-metal wire-based) electrode and the membrane material. The major drawback is the contamination of the inner filling solution due to the variation in ionic strength, due to evaporation of solution, interfering ions, membrane delamination due to repetitive usage, and difficulty in device miniaturization[8].

It is therefore necessary to develop an ISE without an inner filling solution, which can otherwise degrade device performance. A thin water layer often forms between the conductive

material layer and the ion-selective membrane (ISM), acting as an interfacial barrier to charge transport and adversely affecting selectivity, as interfering ions may become trapped and alter the measured potential. Hence, the selection of a suitable transducing layer as a solid contact, replacing the inner filling solution, is crucial for enhancing ion-to-electron conversion efficiency. At the solid contact ion-selective membrane interface, charge carriers are unevenly distributed, where electrons or holes in the solid-contact layer electrostatically interact with cations or anions in the membrane, leading to the formation of an electrical double layer. Enhancing this interfacial phenomenon relies largely on increasing the double-layer capacitance, which can be achieved by maximizing the contact area between the solid-contact layer and the sensing membrane[6]. As a result, a variety of micro and nanostructured materials with high surface areas have been widely investigated as effective ion-to-electron transducers. The use of metal oxide macro- and nanostructured materials as solid-contact layers for ion-to-electron transduction is primarily due to their high surface area and high redox activity. High surface area results from the nanometer size of the particles and pores present in the material structure. High redox activity is due to the electronics and ionic conductivity of the material.

Various materials, including semiconductor metal oxides (Fe_2O_3 , Ni_2O_3), transition metal dichalcogenides (MoS_2), conducting polymers (PEDOT, polyaniline, POT), carbon-based materials (graphene, CNT, reduced graphene oxide), are investigated. Metal oxide materials are often chosen as electrode materials due to the ability of the material to store energy by redox reactions. They possess high electron mobility, chemical stability, and high capacitance.

SnO_2 is an n-type, wide band gap (3.6 eV) semiconductor material with excellent physical, chemical, and thermal stability. SnO_2 has been used in various applications due to its ease of synthesis and formation of versatile morphologies. SnO_2 has faster charge transfer kinetics, enhancing the electrochemical response, and it has sufficient conductivity to mediate efficient electron transfer from the ion-selective membrane to the electrode substrate. SnO_2 is resistant to corrosion, oxidation, and degradation under normal electrochemical conditions. In addition, SnO_2 has a non-stoichiometric oxygen composition, ie SnO and Sn_3O_4 , which is an added advantage for sensing applications. Nanostructured metal oxide has a high density of trapped charged oxygen species (O_2^- , O^- , O^{2-}), resulting in the formation of a surface charged layer in terms of electron depletion (n-type) or hole accumulation layer (p-type). SnO_2 has low electrical conductivity due to its intrinsic low carrier density and mobility, and can be tailored by making a composite with rGO. Incorporation of SnO_2 nanostructures onto rGO sheets significantly enhances the conductivity of the material. The poor sensitivity of SnO_2 is

compensated by rGO, which together acts as an active species for analyte detection. The sensing behavior depends on the microstructural properties of SnO₂ and rGO, which act as an ion-to-electron transducer. Graphene, a two-dimensional sheet of sp²-hybridized carbon atoms, has attracted attention in various applications due to its unique physical and chemical properties. Preparation of high-quality pristine graphene is often carried out by CVD, epitaxial growth on SiC, which is carried out at high temperature, vacuum, and inert gas conditions. Reduced Graphene oxide (rGO) can be synthesized via chemical reduction of graphene oxide, which itself is made by oxidizing graphite powder by the modified Hummers method[9]. GO offers a high surface area with abundant active sites due to oxygen-containing functional groups, making it hydrophilic. GO can be functionalized with metal oxides[10–12].

Here we report SnO₂/rGO composites as an ion-to-electron transducer for nitrate detection. This composite is highly studied, as it combines high surface area and conductivity of GO and semiconducting, electrochemical, and catalytic properties of SnO₂. SnO₂ is prepared by the hydrothermal method, which is then made a composite with GO by a sonochemical synthesis approach. A higher concentration of GO is added to SnO₂ to form SnO₂/rGO composite. The detailed investigation of synthesized composites' structural, morphological, and electrochemical characterization showed that incorporation of SnO₂ into rGO tailors the characteristics of the composites to be used as an ion-to-electron transducer.

Our previous studies demonstrated the use of Ni₂O₃/rGO and Ag-/Fe₂O₃/rGO nanocomposites as ion-to-electron transducer layers for potentiometric nitrate sensing, where the electrochemical response was strongly influenced by the intrinsic redox activity of the metal oxides through the Ni³⁺/Ni²⁺ and Fe³⁺/Fe²⁺-redox couples. In contrast, SnO₂ is comparatively redox inactive within the operating potential window and therefore does not exhibit pronounced faradaic peaks during cyclic voltammetry. Rather than functioning as a redox-active sensing material, the SnO₂/rGO composite serves as an efficient solid-contact ion-to-electron transducer by providing a high interfacial capacitance, improved electrical conductivity through the incorporation of rGO, reduced susceptibility to water-layer formation, and enhanced potential stability. Consequently, this work explores a fundamentally different transduction strategy in which the analytical response originates from stable potentiometric signal transduction rather than faradaic electrochemical reactions. This distinction represents the principal novelty of the present study and demonstrates the suitability of SnO₂/rGO as a robust solid-contact material for long-term potentiometric nitrate sensing.

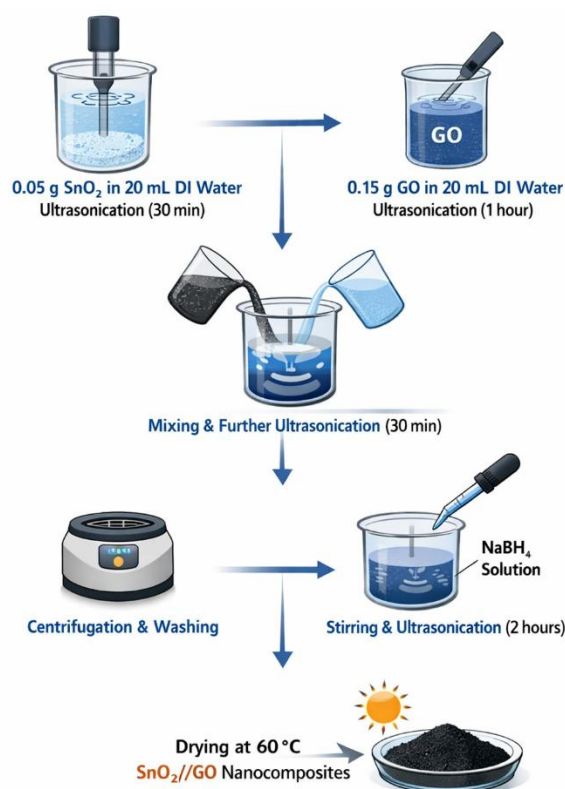
Materials and methods

Synthesis of SnO₂

SnO₂ was synthesized using the procedure described below. Initially, 1.4g of SnCl₂·2H₂O was dissolved in 80 ml of deionized water and allowed to stir for 3 min. 0.5g of CTAB was added to the above solution and stirred further for 60 min. Subsequently, 0.42g of Urea is added and stirred for 3h. The resulting reaction mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated to 180°C for 16h, and air cooled to room temperature. Finally, the obtained reaction solution was washed with water and dried at 100°C overnight.

Synthesis of SnO₂/rGO composites

SnO₂/rGO nanocomposites were prepared in a 1:3 weight ratio by the wet chemical method assisted by ultrasonication. Scheme 1 depicts the schematic representation of the synthesis of SnO₂/rGO composites. In this typical synthesis, 0.05g of SnO₂ nanoparticles were dispersed in 20 mL of deionized water by ultrasonication for 30 min. Separately, 0.15g of GO was dispersed in 20 ml of DI water and ultrasonicated for 1 hour to ensure uniform exfoliation and dispersion. The SnO₂ dispersion is added to the GO dispersion under continuous stirring, followed by further ultrasonication for 30 minutes to obtain a homogenously mixed suspension. Freshly prepared sodium borohydride (NaBH₄) solution, approximately two times the weight of GO, was added slowly by preparing it for 10 mL to the mixture. The stirred mixture was stirred and ultrasonicated for an additional 2 h. The resulting SnO₂/rGO nanocomposites were then collected by centrifugation, washed thoroughly with water to remove unreacted reagents, and dried at 60°C.



Scheme 1: Schematic representation of the synthesis of SnO₂/rGO composites

It should be noted that the CTAB-assisted hydrothermal method was employed exclusively for the synthesis of SnO₂ nanoparticles. The SnO₂/rGO nanocomposite was subsequently fabricated by dispersing the hydrothermally synthesized SnO₂ nanoparticles with graphene oxide, followed by an ultrasonication-assisted wet chemical reduction process using NaBH₄. This distinction is important because the hydrothermal process was used only for the preparation of the SnO₂ nanoparticles, whereas the composite formation was achieved through a separate wet chemical reduction step.

Preparation of ISM cocktail

ISM cocktails were prepared by mixing Methyltriphenylphosphonium bromide (0.2 wt%, 2-nitrophenyloctyl ether 16.25 wt%, polyvinyl chloride 5.75 wt%, tetradodecylammonium nitrate 1.5 wt% in 74.3wt% tetrahydrofuran and refrigerated at 20 °C before use.

Characterization

The crystalline structure of the synthesized samples was analysed using an X-ray diffractometer (ARL EQUINOX 3000, Thermo Fisher Scientific Ltd.). Fourier transform infrared (FTIR) spectra were recorded using a JASCO FTIR-6300 spectrophotometer (JASCO, Japan). Raman spectra were obtained using a WiTec alpha300 Raman microscope (WiTec

GmbH, Ulm, Germany). The morphology of the synthesized nanocomposites was examined using field-emission scanning electron microscopy (FESEM) (Thermo Fisher FEI QUANTA 250 FEG). Electrochemical measurements, including cyclic voltammetry (CV) and open-circuit potentiometry (OCP), were carried out using a CHI 680 Electrochemical Workstation (CH Instruments, Inc., Austin, TX, USA).

Electrochemical measurements for the detection of NO_3^-

A polyester conductive substrate (PCS) was chosen as a substrate for the electrochemical studies. The active sensing area of the coated electrode on the printed circuit substrate (PCS) was $0.5 \text{ cm} \times 0.5 \text{ cm}$, corresponding to an effective area of 0.25 cm^2 . Before measurements, PCS electrodes were washed with ethanol and deionized water. The electrodes were prepared by mixing active material: PVDF: Carbon black in a 70:10:20 ratio in $100 \mu\text{L}$ N-Methyl-2-pyrrolidone, and mixed into a paste and applied to a cleaned substrate and dried at 80°C . The prepared ISM cocktail was added to the active material-coated electrode. $10 \mu\text{L}$ of ISM is dropped onto the active material-coated substrate and is allowed to dry under vacuum in a desiccator. All electrochemical measurements were carried out using a Ag/AgCl (3 M KCl) reference electrode (Indian make 60 mm), a platinum wire counter electrode (Electrode 0.5 mm, 75mm Teflon body with Brass Gold, Plated Connector, and the fabricated working electrode. Phosphate buffer solution at a pH of 7.4 was used as a medium for the electrochemical studies. A phosphate buffer solution (PB, pH 7.4) was prepared by dissolving 20.214 g of sodium phosphate dibasic heptahydrate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$) and 3.394 g of sodium phosphate monobasic monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) in distilled water. The pH was adjusted to 7.4 using dilute HCl or NaOH, and the final volume was made up to 1 L with distilled water. Cyclic voltammetry measurements and open-circuit potentiometry measurements were carried out to study the behaviour of the electrode material towards the detection of nitrate ions.

Results and discussion

X-ray diffraction analysis

The crystallographic structure and phase composition of SnO_2 and SnO_2/rGO nanocomposites were analysed using X-ray diffraction analysis (Fig.1). Pure SnO_2 exhibited sharp and well defined diffraction peaks at $2\theta = 26.7^\circ, 33.9^\circ, 38.4^\circ, 52.03^\circ, 62.41^\circ, 66.11^\circ, 71.82^\circ, 71.8^\circ, 79.22^\circ, 84.62^\circ$, and 90.97° , which are indexed to the (110), (101), (111), (211), (301), (320), (321), (410), and (411) planes of tetragonal rutile SnO_2 (JCPDS No. 41-1445), confirming its

high crystallinity and phase purity [15][16]. Notably, the diffraction peak observed at 52.03° appears as the most intense peak, diverging from the standard SnO_2 profile with a dominant peak of (110). The unusual intensity distribution is due to the preferential crystallographic orientation along the (211) plane, likely induced by the utilization of CTAB as a capping agent during hydrothermal synthesis. In SnO_2/rGO nanocomposites, all the characteristic peaks of SnO_2 are retained, confirming that incorporation of rGO into SnO_2 structures did not affect the crystalline structure of SnO_2 . Interestingly, the peak appearing at 26.7° is significantly increased compared to pure SnO_2 , indicating strong interfacial interaction between SnO_2 and rGO matrix. Additionally, two distinct peaks appeared at 10.34° and 43.04° in the SnO_2/rGO pattern. The peak at 10.34 corresponds to the (001) plane of graphene oxide, which is due to the large interlayer spacing owing to the oxygen group and water molecules[17]. This peak is raised due to the presence of a residual oxygenated functional group or partial reduction. Broad peak at 43.04° is attributed to (100) plane of reduced graphene oxide, which represents in-plane ordering of sp^2 carbon atoms, confirming partial restoration of graphitic structure during the reduction process.

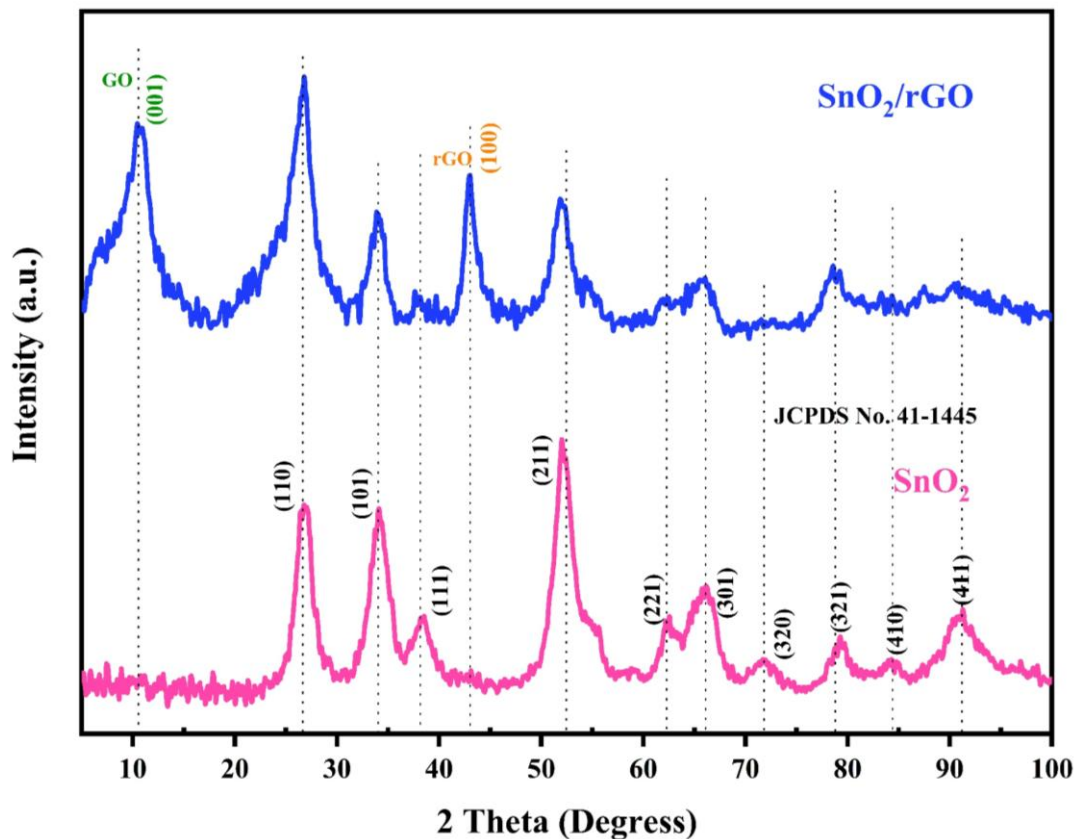


Fig. 2. XRD patterns of pristine SnO₂ nanoparticles and the SnO₂/rGO nanocomposite

Fourier transform Infrared spectroscopy

The Fourier Transform Infrared (FTIR) spectra of pristine SnO₂ (24 h) and SnO₂/rGO nanocomposite are presented in Fig. 2, confirming the formation and interaction of the constituent materials. In the spectrum of SnO₂, a broad absorption band observed in the range of $\sim 3200\text{--}3500\text{ cm}^{-1}$ is attributed to O–H stretching vibrations of adsorbed water molecules and surface hydroxyl groups, while the band near $\sim 1600\text{ cm}^{-1}$ corresponds to H–O–H bending vibrations[18]. A prominent and intense peak appearing in the region of $\sim 500\text{--}700\text{ cm}^{-1}$ is assigned to Sn–O–Sn stretching vibrations, confirming the formation of tin oxide [19, 20]. In the case of the SnO₂/rGO nanocomposite, the O–H stretching band appears broadened, indicating strong interfacial interaction between SnO₂ nanoparticles and the rGO sheets. Additionally, the emergence of weak bands around $\sim 2900\text{ cm}^{-1}$ is attributed to C–H stretching vibrations, while the peak near $\sim 1550\text{--}1600\text{ cm}^{-1}$ corresponds to C=C skeletal vibrations of the graphene structure. A subtle band in the range of $\sim 1200\text{--}1300\text{ cm}^{-1}$ is associated with C–O stretching, suggesting the presence of residual oxygen-containing functional groups[17]. Notably, the Sn–O–Sn vibration band in the composite is retained but exhibits a slight shift and reduction in intensity, indicating successful anchoring of SnO₂ onto the rGO matrix. These spectral modifications confirm the formation of the SnO₂/rGO nanocomposite with strong interfacial coupling between the metal oxide and carbon framework.

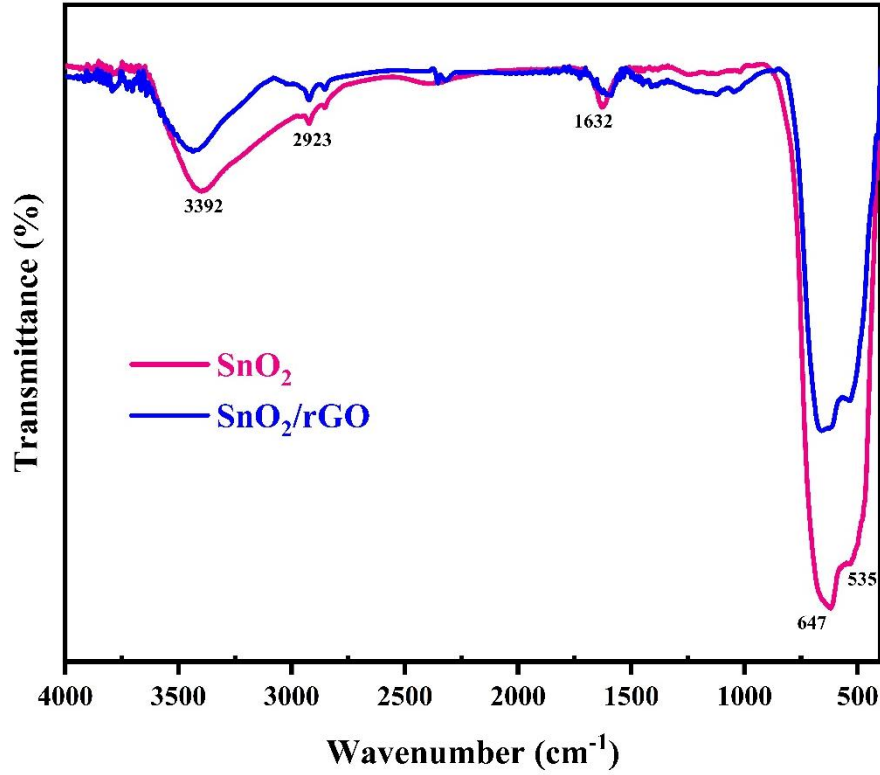


Fig.2 FTIR Spectra of pristine SnO₂ nanoparticles and the SnO₂/rGO nanocomposite
Raman analysis

The Raman spectra of pristine SnO₂ and the SnO₂/rGO nanocomposite (Fig. 3) exhibit distinct vibrational features that confirm phase formation and successful hybridization. In the pristine SnO₂ spectrum, prominent peaks are observed at ~ 308 , ~ 628 , and ~ 775 cm⁻¹. The strong and sharp band at ~ 628 cm⁻¹ corresponds to the A_{1g} mode, which is characteristic of the rutile tetragonal phase of SnO₂ and indicates good crystallinity of the synthesized oxide. The weaker bands around ~ 308 cm⁻¹ and ~ 775 cm⁻¹ can be attributed to E_g and B_{2g} modes, respectively. For the SnO₂/rGO nanocomposite, the SnO₂-related peak near ~ 632 cm⁻¹ is retained but appears broadened and slightly reduced in intensity compared to pristine SnO₂. This suggests strong interfacial interaction between SnO₂ nanoparticles and the rGO matrix, along with possible phonon confinement effects due to reduced crystallite size.

Additionally, new prominent peaks emerge at ~ 1358 cm⁻¹ and ~ 1583 cm⁻¹, corresponding to the D and G bands of the carbon component in the SnO₂/rGO nanocomposite. The D band is associated with defect-induced vibrations of sp² carbon domains, while the G band arises from the in-plane stretching of sp² carbon atoms. The calculated intensity ratio (I_D/I_G), was 0.8157, indicating the presence of structural defects together with graphitic sp² carbon domains within

the rGO framework. The appearance of these characteristic D and G bands, along with the calculated I_D/I_G ratio, confirms the successful incorporation of the rGO component into the SnO_2/rGO nanocomposite.

Furthermore, the appearance of a band around $\sim 1136\text{ cm}^{-1}$ in the composite may be attributed to C–O or residual oxygen-containing functional groups, suggesting incomplete reduction of graphene oxide. Overall, the coexistence of SnO_2 vibrational modes and characteristic rGO bands, along with peak broadening and intensity changes, confirms the successful formation of the SnO_2/rGO nanocomposite and strong electronic coupling between the oxide nanoparticles and the conductive carbon network.

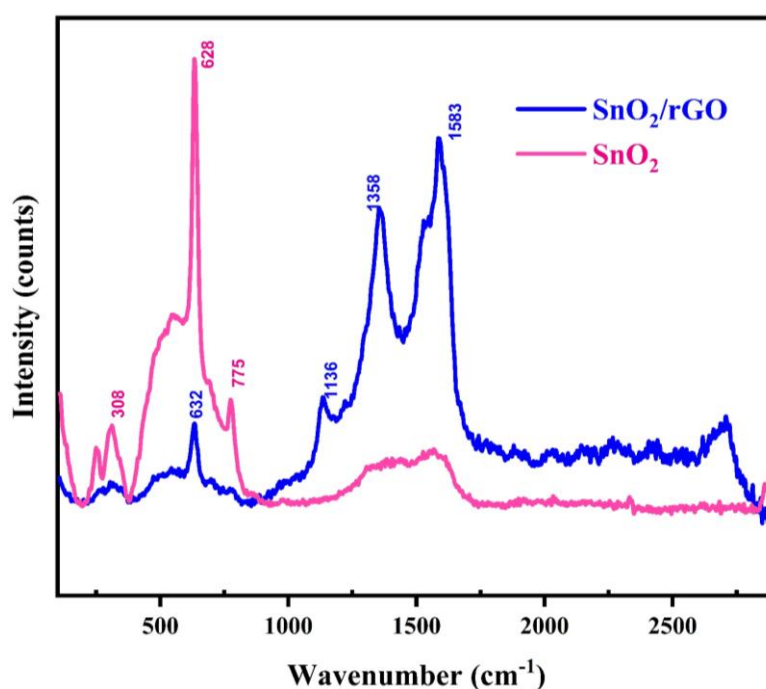


Fig.3 Raman Spectra of pristine SnO_2 nanoparticles and the SnO_2/rGO nanocomposite

Microscopic analysis

Field Emission Scanning Electron Microscopy (FESEM) was employed to examine the surface morphology and microstructural characteristics of pure SnO_2 and SnO_2/rGO nanocomposites at different magnifications. The FESEM images of pure SnO_2 reveal a dense assembly of uniformly distributed nanostructures covering the entire surface, as in Fig.4. At lower and intermediate magnifications, SnO_2 appears predominantly as quasi-spherical to irregularly shaped nanoparticles forming a compact and continuous network. The individual particles are

in the nanometer size range and are closely packed, resulting in the formation of secondary agglomerates due to high surface energy. This morphology is typical of hydrothermally synthesized metal oxides and is influenced by the presence of CTAB as a capping and structure-directing agent, which restricts excessive particle growth and promotes controlled nucleation. At higher magnifications, the granular and textured surface of SnO₂ is clearly visible, providing a high surface area. Occasional larger fused domains suggest partial oriented attachment or Ostwald ripening during prolonged hydrothermal treatment, which correlates well with the preferential (211) crystallographic orientation observed in XRD analysis.

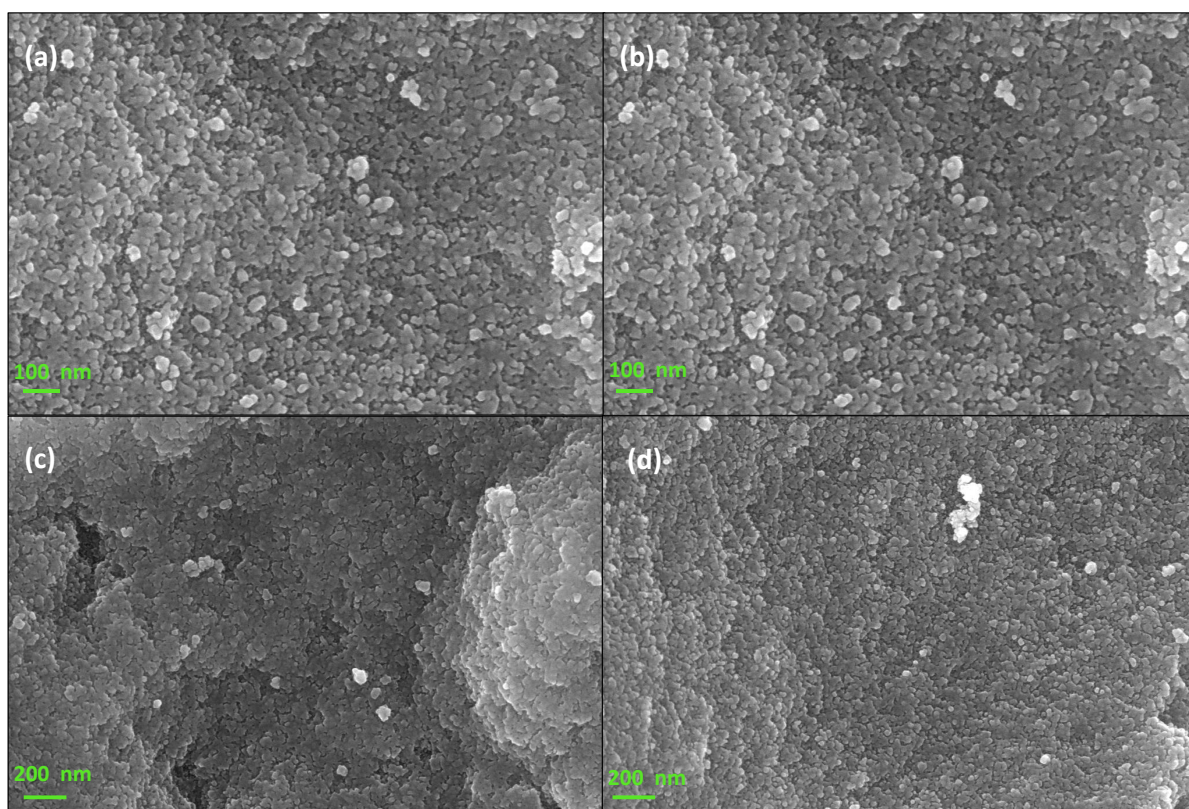


Fig.4 FESEM images of pristine SnO₂ nanoparticles

In contrast, the FESEM images of the SnO₂/rGO nanocomposites exhibit a markedly different morphology (Fig.5). At lower magnifications of 100 nm and 200 nm, the composite shows a typical wrinkled, crumpled, and sheet-like structure, characteristic of reduced graphene oxide (rGO). The rGO sheets are loosely stacked and folded, forming an interconnected three-dimensional network with abundant voids and open channels. This morphology effectively suppresses restacking of graphene layers and enhances surface accessibility.

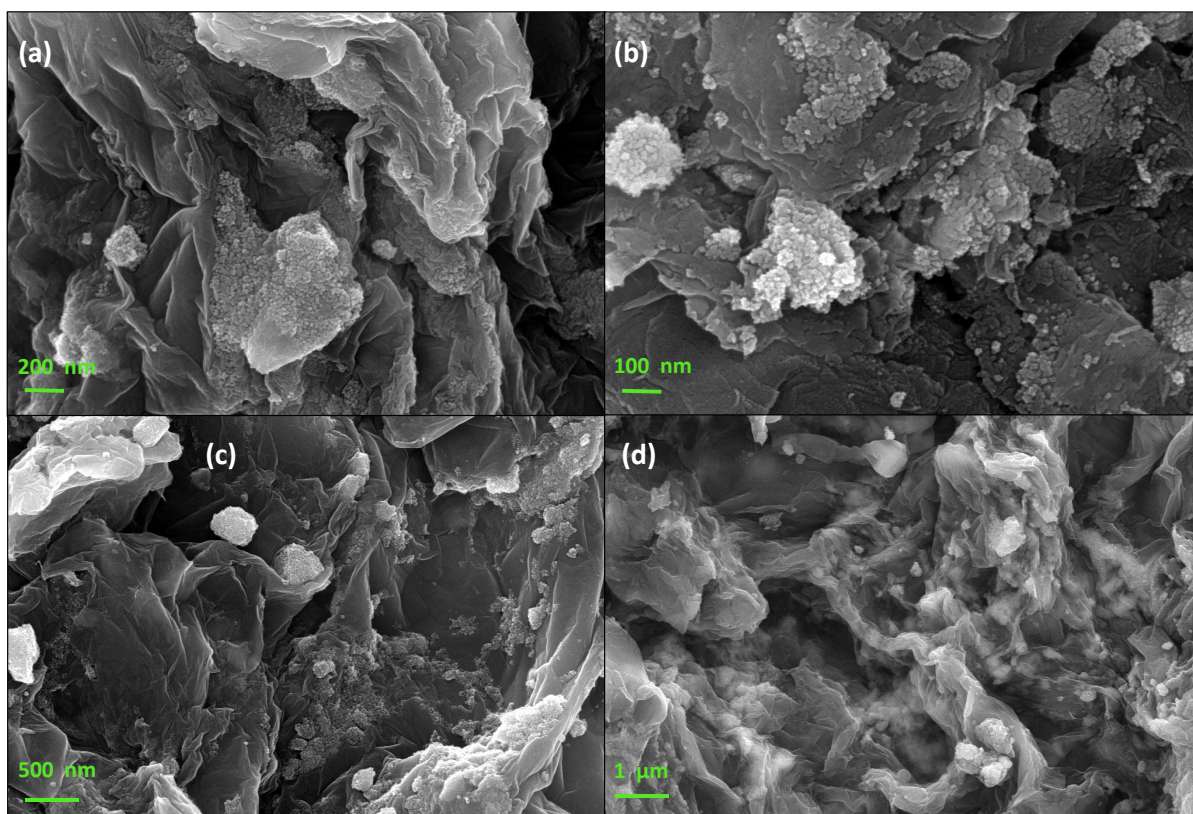


Fig.5 FESEM images of SnO₂/rGO nanocomposite

At higher magnifications 1 μm , SnO₂ nanoparticles are clearly observed to be uniformly anchored onto the surface of rGO sheets. The nanoparticles retain their nanoscale dimensions and are homogeneously distributed without severe agglomeration, indicating strong interfacial interaction between SnO₂ and rGO. The effective dispersion and intimate contact are attributed to the ultrasonication-assisted wet chemical synthesis and chemical reduction using NaBH₄, which facilitates firm attachment of SnO₂ onto the rGO matrix. In some regions, small clustered domains of SnO₂ are visible, likely originating from localized nucleation during the reduction process.

Overall, the FESEM analysis demonstrates that while pure SnO₂ exhibits a compact and agglomerated nanoparticulate morphology, the incorporation of rGO results in a well-dispersed hybrid structure where SnO₂ nanoparticles are uniformly distributed on conductive and wrinkled rGO sheets. This structural transformation enhances porosity, prevents nanoparticle aggregation, and improves interfacial charge transfer, which is consistent with the XRD results and is expected to significantly improve the functional performance of the SnO₂/rGO nanocomposites in sensing, catalytic, and electrochemical applications.

In some regions, larger aggregated domains composed of fused nanoparticles are visible, indicating partial oriented attachment or Ostwald ripening during prolonged hydrothermal treatment at 180°C. This observation is in good agreement with the preferential crystallographic orientation along the (211) plane observed in the XRD analysis, suggesting a correlation between crystal growth direction and morphological evolution.

Overall, the FESEM results confirm that the synthesized SnO₂ exhibits a nanocrystalline, highly dense, and porous-like morphology, which complements the XRD findings of high crystallinity and phase purity. The nanoscale particle size and interconnected architecture are expected to enhance charge transport and surface-related properties.

Energy-dispersive X-ray spectroscopy (EDS) was performed to investigate the elemental composition of the synthesized SnO₂ and SnO₂/rGO nanocomposites, as shown in Fig. 6. The EDS spectrum of pristine SnO₂ (Fig. 6a) exhibits only Sn and O peaks, confirming the successful formation of tin oxide without detectable impurity elements. The corresponding elemental analysis reveals weight percentages of 84.77% Sn and 15.23% O. In contrast, the EDS spectrum of the SnO₂/rGO nanocomposite (Fig. 6b) clearly shows the presence of C, O, and Sn, confirming the successful incorporation of reduced graphene oxide with SnO₂. The high carbon content (52.47 wt%) originates from the rGO sheets, while the presence of Sn and O further verifies the formation of the SnO₂/rGO composite. These results support the successful synthesis of the nanocomposite and are in good agreement with the XRD, FTIR, and Raman analyses.

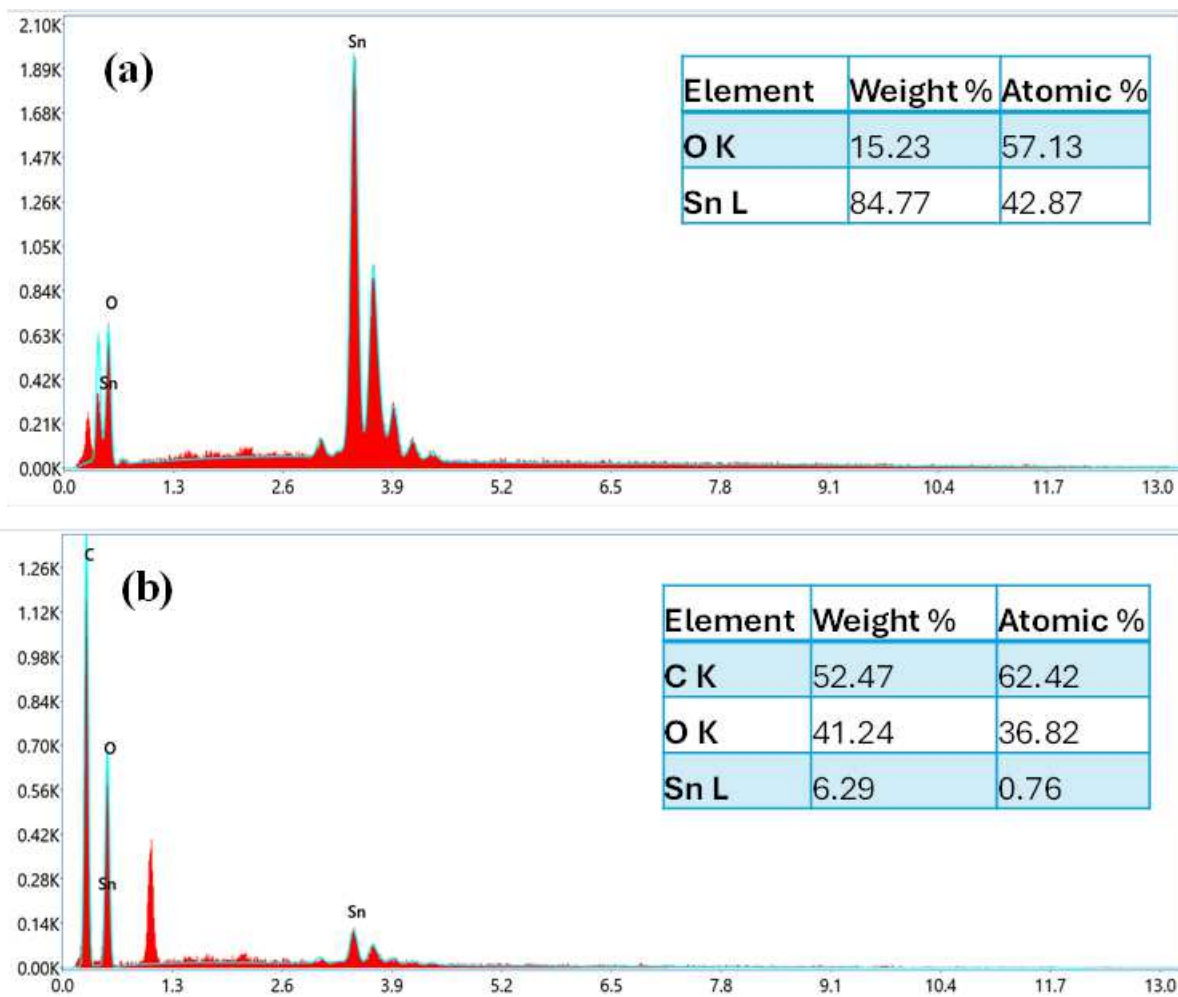


Fig.6 EDS spectra and elemental composition of (a) pristine SnO₂ nanoparticles and (b) SnO₂/rGO nanocomposite.

3. Electrochemical Studies

The electrochemical behaviour of SnO₂, ISM SnO₂, SnO₂/rGO, and ISM SnO₂/rGO- modified electrodes in phosphate-buffered solution (PBS) was investigated by cyclic voltammetry (CV) studies. The CV measurements were recorded in the potential window of -1.0 V to +1.5 V (vs. Ag/AgCl) at various scan rates (10, 30, 50, 80, and 100 mV/s), as illustrated in Fig.7. The CV curves of SnO₂ and ISM SnO₂ exhibit quasi-rectangular CV curves, indicating capacitive behaviour with no pronounced faradaic redox peaks within the investigated potential window. As the scan rate increases, the current increases, suggesting a surface-controlled process. There is a notable increase in current response in SnO₂/rGO and ISM SnO₂/rGO modified electrodes, demonstrating the beneficial effect of incorporating rGO into the solid-contact layer.

The SnO₂/rGO electrode exhibited a larger enclosed CV area and higher current response than the pristine SnO₂ electrode. This enhancement is attributed to the excellent electrical conductivity of the rGO network, which provides efficient electron transport pathways and increases the interfacial capacitance of the solid-contact layer. The ISM-coated SnO₂/rGO electrode also exhibited an increased current response, indicating that the combined effect of the SnO₂/rGO composite and the ion-selective membrane provides a stable and efficient ion-to-electron transduction interface suitable for potentiometric sensing.

The CV curves for all electrodes show increasing current with increasing scan rate, indicating a predominantly surface-controlled capacitive charge-storage process. The ISM SnO₂/rGO electrode maintains its quasi-rectangular profile even at higher scan rates, demonstrating good electrochemical stability and efficient charge-storage capability. Furthermore, the linear relationship between the current response and scan rate confirms that the electrochemical behaviour is governed primarily by surface-controlled capacitive processes. These characteristics are desirable for solid-contact potentiometric ion-selective electrodes because they promote efficient ion-to-electron transduction, high interfacial capacitance, and stable potential generation during open-circuit measurements.

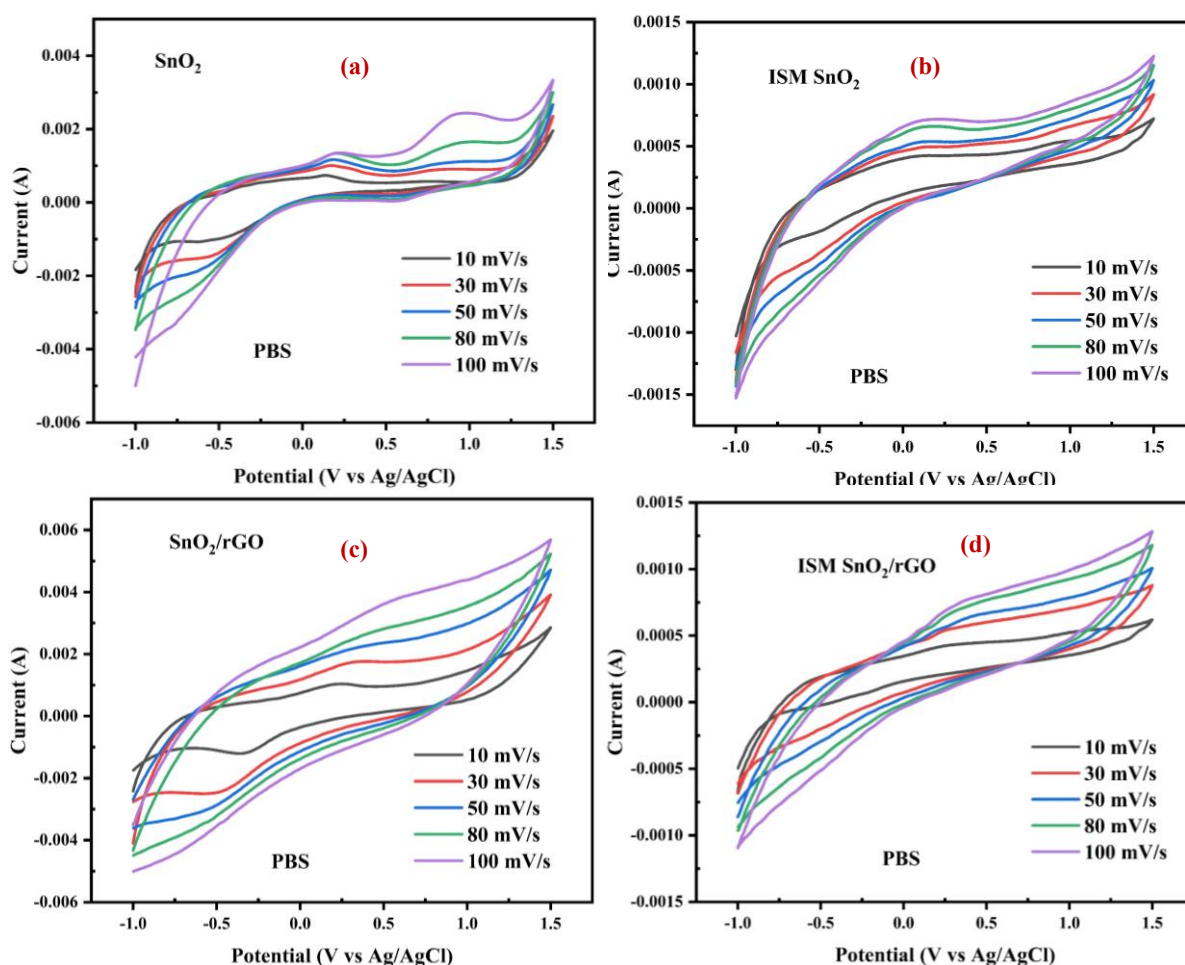
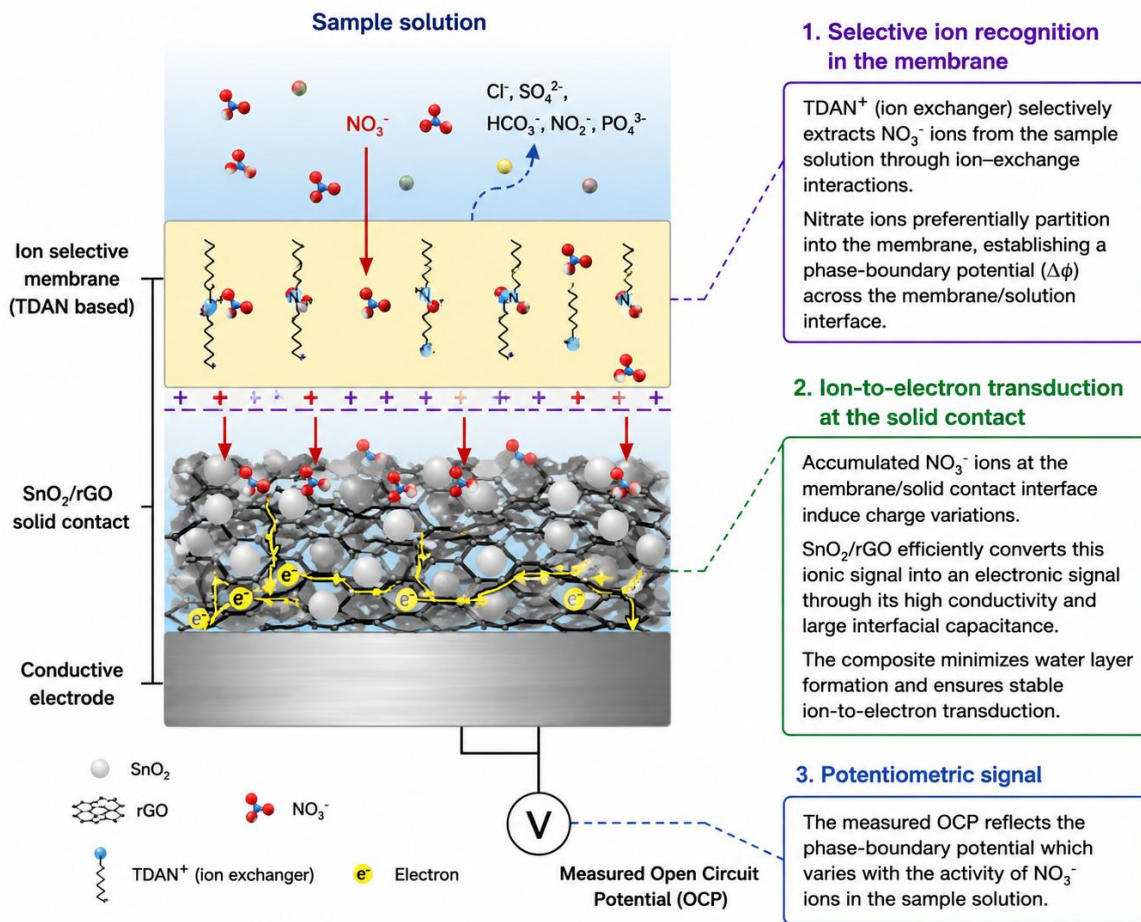


Fig. 7. Cyclic voltammograms of (a) pristine SnO_2 , (b) ion-selective membrane (ISM)-coated SnO_2 , (c) SnO_2/rGO nanocomposite, and (d) ISM-coated SnO_2/rGO electrodes recorded in phosphate-buffered solution (PBS, pH 7.4) over the potential range of -1.0 to $+1.5$ V (vs. Ag/AgCl) at scan rates of 10, 30, 50, 80, and 100 mV s^{-1} .

The sensing mechanism of the proposed ISM– SnO_2/rGO electrode follows the well-established operating principle of solid-contact ion-selective electrodes (SC-ISEs). Unlike amperometric or voltammetric sensors, the analytical response of the present device is obtained under open-circuit conditions, where the measured potential originates from the selective recognition of nitrate ions and the establishment of a phase-boundary potential at the membrane/solution interface, rather than from faradaic electrochemical reactions. A schematic representation of the proposed sensing mechanism is illustrated in Scheme 2.



Scheme 2. Schematic illustration of the potentiometric sensing mechanism of the proposed ISM-SnO₂/rGO solid-contact nitrate sensor, showing selective nitrate ion extraction by the TDAN-based ion-selective membrane, formation of the phase-boundary potential, and ion-to-electron transduction through the SnO₂/rGO solid-contact layer, resulting in a stable open-circuit potential (OCP) response.

Upon immersion of the sensor in a nitrate-containing solution, the TDAN-based ion-selective membrane (ISM) selectively extracts nitrate ions from the sample through ion-exchange interactions. Due to the lipophilic nature of TDAN, nitrate ions preferentially partition into the membrane phase, resulting in the development of a phase-boundary potential at the membrane/solution interface. The magnitude of this potential is directly related to the activity of nitrate ions in the sample solution and constitutes the fundamental sensing principle of the proposed potentiometric sensor.

The extracted nitrate ions accumulate at the interface between the ion-selective membrane and the SnO₂/rGO solid-contact layer. The SnO₂/rGO nanocomposite functions as an efficient ion-to-electron transducer, converting the ionic charge variations within the membrane into a stable

electronic signal. The incorporation of reduced graphene oxide (rGO) enhances the electrical conductivity of the composite and provides continuous electron transport pathways, while SnO₂ offers a chemically stable, high-surface-area interface with excellent interfacial capacitance. These synergistic properties facilitate efficient ion-to-electron transduction, suppress the formation of an undesirable water layer, minimize potential drift, and improve the long-term stability of the potentiometric response.

The cyclic voltammetry results further support the role of the SnO₂/rGO composite as a solid-contact transducer. The CV curves exhibit predominantly capacitive behaviour without distinct faradaic redox peaks, indicating that the electrochemical response is governed primarily by charge storage at the interface rather than electrochemical nitrate reduction. The larger enclosed CV area observed for the SnO₂/rGO electrode compared with pristine SnO₂ demonstrates its enhanced interfacial capacitance and improved charge-storage capability, both of which are essential for stable potentiometric signal transduction.

Our previous studies employing Ni₂O₃/rGO and Ag/Fe₂O₃/rGO nanocomposites exhibited distinct faradaic redox peaks owing to the intrinsic redox activity of the Ni³⁺/Ni²⁺ and Fe³⁺/Fe²⁺ couples. In contrast, SnO₂ is comparatively redox inactive within the investigated potential window and therefore does not exhibit pronounced faradaic behaviour. Consequently, the present work employs open-circuit potentiometry (OCP), where the analytical response is governed by selective ion recognition, phase-boundary potential formation, and efficient ion-to-electron transduction rather than electrochemical nitrate reduction.

Overall, the enhanced sensing performance of the ISM–SnO₂/rGO electrode arises from the synergistic combination of selective nitrate recognition by the TDAN-based ion-selective membrane and the excellent ion-to-electron transduction capability of the SnO₂/rGO solid-contact layer, resulting in improved sensitivity, enhanced potential stability, and reliable potentiometric nitrate detection.

Potentiometric response and sensitivity towards nitrate ions.

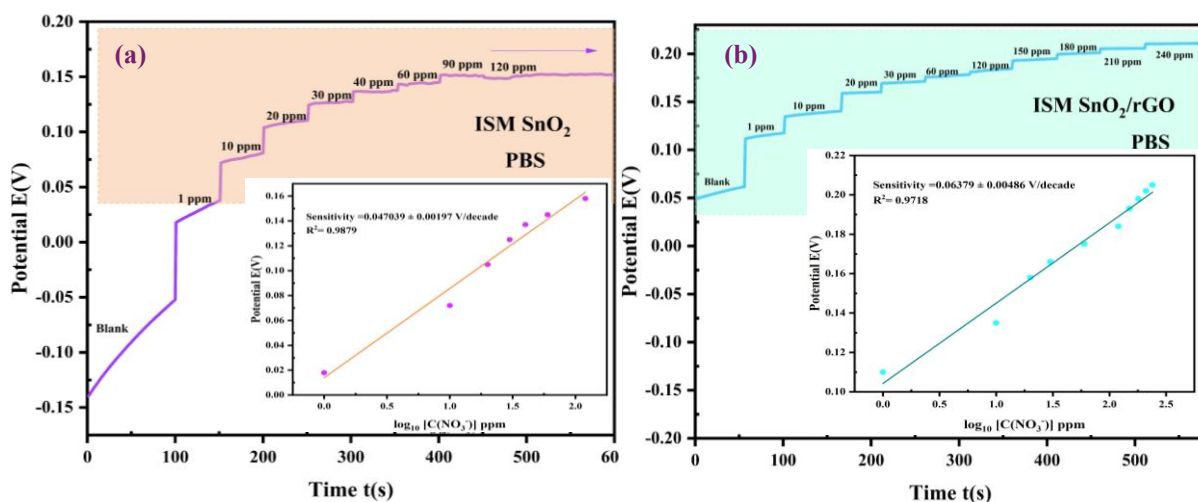


Fig.8 Open-circuit potential (OCP) response of the (a) ISM-SnO₂ (b) ISM-SnO₂/rGO electrode toward different nitrate concentrations, demonstrating the linear potentiometric response and sensitivity of the sensor.

The potentiometric performance of the ISM-modified SnO₂ and SnO₂/rGO electrodes was systematically investigated in phosphate-buffered solution (PBS, pH 7.4) upon successive additions of nitrate ions (NO₃⁻) (Fig.8). Both systems exhibited a clear, stepwise increase in open-circuit potential (OCP), reflecting effective ion recognition by the membrane and efficient signal transduction. For the ISM-SnO₂ electrode, the potential exhibits a clear, stepwise increase with each addition of NO₃⁻. The potential shifted from approximately -0.15 V to 0.17 V across the concentration range of 1 to 120 ppm, with a sensitivity of 0.04703 ± 0.00197 V/decade and a strong linear correlation (R² = 0.9879). In comparison, the ISM-SnO₂/rGO electrode demonstrated an extended detection range of 1 to 240 ppm, with the potential increasing up to ~0.21 V. Notably, the sensitivity improved to 0.06379 ± 0.00486 V/decade (R² = 0.9718), indicating enhanced charge transfer dynamics. This improved response is attributed to the incorporation of reduced graphene oxide (rGO), which provides a high surface area, superior electrical conductivity, and facilitates faster ion-to-electron transduction at the sensing interface. Incorporation of rGO into the ISM-SnO₂ platform significantly improves the electrodes' sensing capabilities, as evidenced by broader detection range, increased sensitivity, and fast potential drifts. This suggests that ISM-coated rGO-based SnO₂ nanostructures are suitable for electrochemical sensing applications.

Electrode Transducer /	Ion exchanger / Membrane	Detection Method	Sensitivity (mV decade ⁻¹)	LOD (M)	Linear Range (M)	Ref.
ZnO:Pt nanocomposite	TDMANO ₃	Potentiometric (SC-ISE)	-62.52	3.2×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-1}$	[21]
CoWSe ₂ nanocomposite	TDMANO ₃	Potentiometric (SC-ISE)	-61.9 ± 0.4	1×10^{-6}	$1 \times 10^{-6} - 7.5 \times 10^{-2}$	[22]
POT-MoS ₂ nanocomposite	TDMANO ₃	Potentiometric (SC-ISE)	-81.76	1.05×10^{-5}	$7.45 \times 10^{-5} - 1.45 \times 10^{-3}$	[23]
Polyaniline (PANI)	TDABr	Potentiometric (SC-ISE)	-58.6 ± 5.2	1.67×10^{-6}	$1 \times 10^{-5} - 1 \times 10^{-1}$	[24]
Conductive nano-Cink (JC81)	TOABr		-58	<10 ⁻⁶	10 ⁻⁹ -2.7	[25]
MWCNT/CuO nanoparticles	TDMANO ₃	Potentiometric (SC-ISE)	-60.41	5.13×10^{-7}	$1 \times 10^{-6} - 1 \times 10^{-1}$	[26]
Co ₃ O ₄ nanoparticles/SPCE	TDMANO ₃	Potentiometric (SC-ISE)	-56.8	1.04×10^{-8}	$1 \times 10^{-7} - 1 \times 10^{-2}$	[27]
PEDOT-C14	TDMANO ₃	Potentiometric (SC-ISE)	-52.2	3.16×10^{-6}	$5 \times 10^{-4} - 1 \times 10^{-1}$	[28]
MCB solid contact	TDMANO ₃	Potentiometric (SC-ISE)	-54.8	2.5×10^{-6}	$5 \times 10^{-5} - 1 \times 10^{-1}$	[29]
Molecular cage ionophore (CAGE-1)	CAGE-1 (chlorotriazine pillared molecular cage)	Potentiometric (ISE)	-53.1 ± 1.4	7.5×10^{-6}	$1.0 \times 10^{-5} - 1.0 \times 10^{-1}$	[30]
Carbon black/RuO ₂ /POT solid contact	Nitrate-selective PVC membrane	Potentiometric (SC-ISE)	≈ -58.8	$\approx 1 \times 10^{-5}$	$1 \times 10^{-5} - 1 \times 10^{-1}$	[31]

Commercial nitrate ISE	Commercial nitrate-selective membrane	Direct potentiometry	−59.2 (near-Nernstian)	3.1×10^{-6}		[32]
Carbon electrode + nitrate ion-selective membrane	TDPA/PVC membrane	Electrochemical Impedance Spectroscopy (EIS)	Not reported in mV decade ^{−1}		5–512 ppm (soil calibration)	[33]
Ag/Fe ₂ O ₃ /rGO	TDAN	Potentiometric (SC-ISE)	$1.426 \mu A \mu M^{-1} cm^{-2}$	0.18 μM	10 to 450 μM	[14]
Ni ₂ O ₃ /rGO	TDAN	Potentiometric (SC-ISE)	$13.3 \mu A/(mg/L)/cm^2$	23.59 mg/L	1 ppm to 200 ppm	[13]
SnO ₂ /rGO (Present work)	TDAN	Potentiometric (SC-ISE)	−63.79 ± 4.86 (after correcting sign)	Add after LOD calculation	1–240 ppm	This work

Practical applicability of ISM–SnO₂/rGO electrode towards nitrate detection:

To evaluate the practical applicability of the proposed ISM–SnO₂/rGO electrode for nitrate sensing, additional analytical performance studies were carried out, including response time, potential stability, repeatability, reproducibility, selectivity, and working concentration range. The potentiometric response shown in Fig. 9 demonstrates a rapid and stable change in potential upon successive additions of nitrate solution. During the measurements, the electrode was allowed to stabilize for approximately 90 s after each concentration change before recording the equilibrium potential, indicating a fast response toward nitrate ions. The electrode exhibited a linear potentiometric response over the nitrate concentration range of 1–240 ppm, with 1 ppm representing the lower limit of the experimentally validated working range.

The short-term stability of the proposed electrode was further evaluated by continuously monitoring the open-circuit potential in a 60-ppm nitrate solution for 60 min, as shown in Fig.

9(a). Only a marginal variation in potential was observed throughout the measurement period, indicating good operational stability and negligible potential drift under constant experimental conditions. The repeatability of the fabricated ISM-SnO₂/rGO electrode was assessed by performing five consecutive potentiometric measurements in 60 ppm nitrate solution using the same electrode. As illustrated in Fig. 9(b), the measured potentials remained highly consistent, confirming excellent repeatability of the sensor response. Furthermore, the reproducibility of the electrode fabrication process was evaluated by preparing five independently fabricated ISM-SnO₂/rGO electrodes under identical conditions and testing each electrode in 60 ppm nitrate solution as in Fig. 9(d). The electrodes exhibited comparable potentiometric responses, demonstrating good reproducibility and reliability of the fabrication procedure.

The selectivity of the proposed electrode was investigated using the Separate Solution Method (SSM) by measuring the open-circuit potential response in separate PBS solutions containing 60 ppm of nitrate and common interfering anions, namely Cl⁻, SO₄²⁻, HCO₃⁻, NO₂⁻, and PO₄³⁻. As presented in Fig. 9(c), The ISM-SnO₂/rGO electrode exhibited the highest potentiometric response toward nitrate ions, while the responses toward the interfering anions followed the order: NO₃⁻ > NO₂⁻ > Cl⁻ > HCO₃⁻ > SO₄²⁻ > PO₄³⁻, indicating the preferential recognition of nitrate ions by the TDAN-based ion-selective membrane. Among the investigated interferents, nitrite exhibited the greatest interference owing to its structural similarity to nitrate, whereas sulfate and phosphate showed the lowest interference, demonstrating the suitability of the proposed sensor for nitrate determination in the presence of common environmental anions.

Although the present work focused on evaluating the sensor performance within the experimentally investigated concentration range, an IUPAC-compliant limit of detection (LOD) was not determined because measurements below 1 ppm were not performed. Therefore, 1 ppm is reported as the lower limit of the experimentally validated linear working range rather than the LOD.

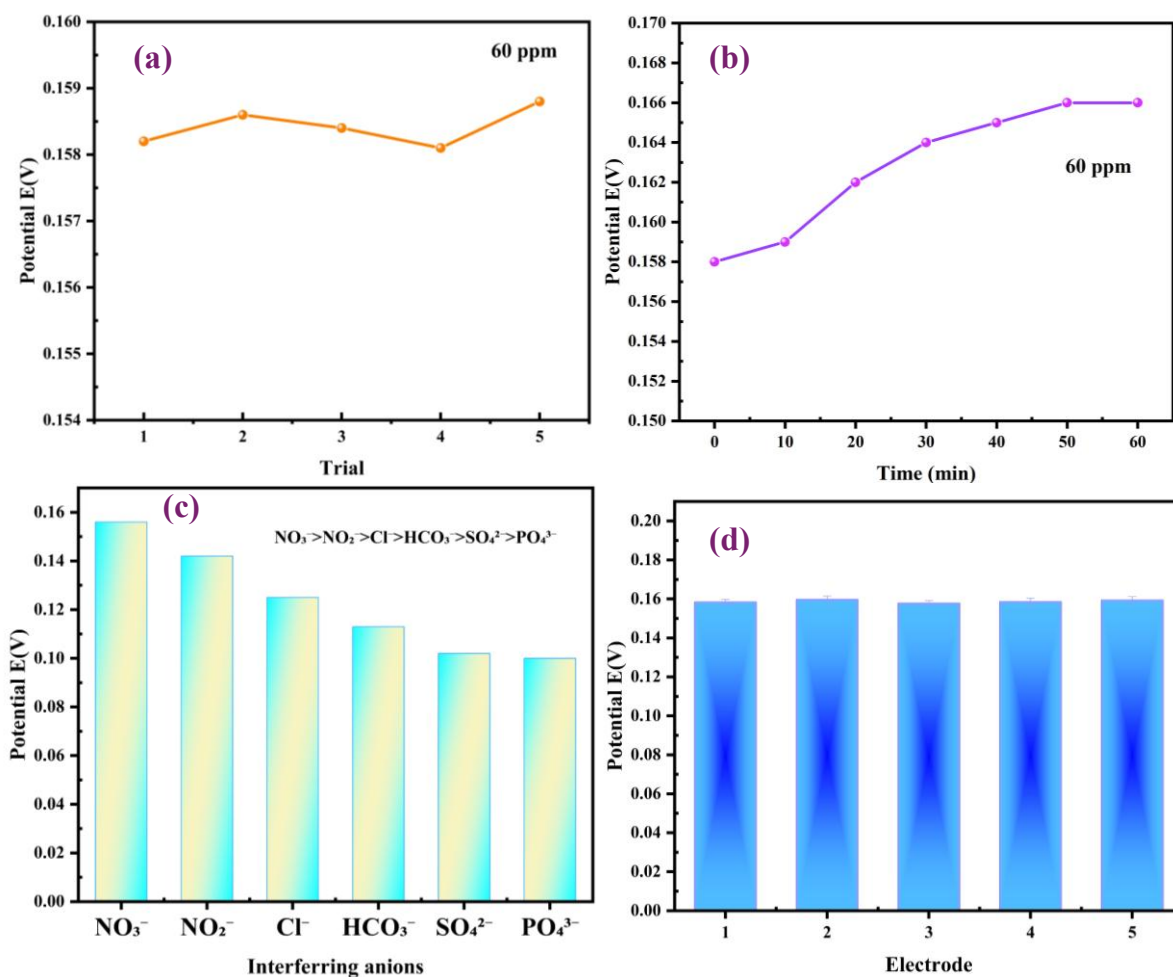


Fig. 9. Practical performance evaluation of the ISM-SnO₂/rGO ion-selective electrode for nitrate sensing: (a) repeatability of five consecutive measurements in 60 ppm nitrate solution; (b) short-term stability of the electrode monitored in 60 ppm nitrate solution for 60 min; (c) potentiometric response toward nitrate and common interfering anions (NO₂⁻, Cl⁻, HCO₃⁻, SO₄²⁻, and PO₄³⁻), each measured separately at 60 ppm in PBS, demonstrating the selectivity of the proposed electrode; and (d) reproducibility of five independently fabricated ISM-SnO₂/rGO electrodes tested under identical experimental conditions in 60 ppm nitrate solution.

Conclusion

A TDAN-based nitrate ion-selective membrane integrated with an SnO₂/rGO solid-contact layer was successfully developed for potentiometric nitrate detection. The proposed ISM-SnO₂/rGO electrode exhibited a sensitivity of 63.79 ± 4.86 mV decade⁻¹ over an experimentally investigated nitrate concentration range of 1–240 ppm, demonstrating a clear and reproducible potentiometric response. The incorporation of rGO enhanced the sensing performance compared with the SnO₂-based electrode, particularly in terms of sensitivity and working

range. The electrode showed good repeatability and reproducibility, confirming the consistency of the fabrication procedure. Selectivity studies further demonstrated a preferential response toward nitrate compared with commonly encountered interfering anions. The electrode also exhibited satisfactory short-term potential stability during continuous OCP measurements. Overall, the combination of SnO₂ nanoparticles and rGO provides a promising solid-contact platform for potentiometric nitrate sensing. The significance of this work lies in demonstrating a simple composite-based electrode architecture with enhanced potentiometric performance for nitrate monitoring. Further studies involving formal IUPAC-compliant LOD determination, EIS characterization, long-term stability, pH effects, and validation using real environmental water samples are planned to establish its practical applicability.

Declaration of competing interest

There are no conflicts to declare

Research Data Policy and Data Availability Statements

All data generated or analyzed during this study are included in this published article.

Funding declaration

The authors declare that no external funding was received for the research, authorship, or publication of this article.

Author contribution

All authors contributed to the study, conceptualization, and design. Material preparation, data collection, validation analysis and investigation of the research data were carried out by Percy J. Sefhra. The original writing was done by Percy J. Sefhra. Review, investigation of research data and editing of the draft are carried out by C. Tharini.

References

1. Singh S, Anil AG, Kumar V, et al (2022) Nitrates in the environment: A critical review of their distribution, sensing techniques, ecological effects and remediation. *Chemosphere* 287
2. Alahi MEE, Mukhopadhyay SC (2018) Detection methods of nitrate in water: A review. *Sensors Actuators, A Phys.* 280:210–221

3. Ryu H, Thompson D, Huang Y, et al (2020) Electrochemical sensors for nitrogen species: A review. *Sensors and Actuators Reports* 2:. <https://doi.org/10.1016/j.snr.2020.100022>
4. Chen X, Zhou G, Mao S, Chen J (2018) Rapid detection of nutrients with electronic sensors: A review. *Environ Sci Nano* 5:837–862. <https://doi.org/10.1039/c7en01160a>
5. Luciani L, Nocera A, Raimondi M, et al (2025) Raman Spectroscopy for Nitrate Detection in Water: A Review of the Current State of Art. *ACS Meas Sci Au* 5:443–460. <https://doi.org/10.1021/acsmmeasuresciau.5c00016>
6. Shao Y, Ying Y, Ping J (2020) Recent advances in solid-contact ion-selective electrodes: Functional materials, transduction mechanisms, and development trends. *Chem Soc Rev* 49:4405–4465. <https://doi.org/10.1039/c9cs00587k>
7. Cattrall RW, Freiser H (1971) Coated wire ion-selective electrodes. *Anal Chem* 43:1905–1906. <https://doi.org/10.1021/ac60307a032>
8. Kim Y, Seo M, Baek S (2025) Ion-selective electrode-based sensors from the macro- to the nanoscale. *Sensors and Actuators Reports* 9:. <https://doi.org/10.1016/j.snr.2024.100258>
9. Zaaba NI, Foo KL, Hashim U, et al (2017) Synthesis of Graphene Oxide using Modified Hummers Method : Solvent Influence. *Procedia Eng* 184:469–477. <https://doi.org/10.1016/j.proeng.2017.04.118>
10. Jung J, Jeong JR, Lee J, et al (2020) In situ formation of graphene/metal oxide composites for high-energy microsupercapacitors. *NPG Asia Mater* 12:. <https://doi.org/10.1038/s41427-020-0230-y>
11. Liu Y, Ying Y, Mao Y, et al (2013) CuO nanosheets/rGO hybrid lamellar films with enhanced capacitance. *Nanoscale* 5:9134. <https://doi.org/10.1039/c3nr02737f>
12. Guo S, Zhang G, Guo Y, Yu JC (2013) Graphene oxide-Fe₂O₃ hybrid material as highly efficient heterogeneous catalyst for degradation of organic contaminants. *Carbon N Y* 60:437–444. <https://doi.org/10.1016/j.carbon.2013.04.058>
13. J. PS, C. T, Sachdev A, E. M (2024) An efficient sensing system using ion-selective membrane on Ni₂O₃/rGO nanocomposite for electrochemical detection of nitrate ions. *J Alloys Compd* 980:173414. <https://doi.org/10.1016/j.jallcom.2023.173414>
14. Sephra PJ, Chandrapagasam T, Sachdev A, Esakkimuthu M (2024) Bifunctional properties of Ag/ α -Fe₂O₃/rGO nanocomposite for supercapacitor and electrochemical nitrate sensing using tetradodecyl ammonium nitrate as ion-selective membrane. *Environ Sci Pollut Res* 31:52886–52904. <https://doi.org/10.1007/s11356-024-34703-x>
15. Osora H, Kolkoma D, Anduwan G, et al (2024) Hydrothermally Grown SnO₂ and SnO₂/rGO Nanocomposite and Its Physio-Electrochemical Studies for Pseudocapacitor Electrode Applications. *J Clust Sci* 35:891–901. <https://doi.org/10.1007/s10876-023-02517-5>
16. ChemistrySelect - 2025 - Anito - Post-synthesis Physical and Hydrothermal Mixing of MnO₂ SnO₂ and rGO Influence on.pdf
17. Velmurugan V, Srinivasarao U, Ramachandran R, et al (2016) Synthesis of tin oxide/graphene (SnO₂/G) nanocomposite and its electrochemical properties for

- supercapacitor applications. *Mater Res Bull* 84:145–151.
<https://doi.org/10.1016/j.materresbull.2016.07.015>
18. Wang Y, Tan L, Wang L (2011) Hydrothermal synthesis of SnO₂ nanostructures with different morphologies and their optical properties. *J Nanomater* 2011:.
<https://doi.org/10.1155/2011/529874>
 19. Zamiri G, Haseeb ASMA, Jagadish P, et al (2022) Three-Dimensional Graphene-TiO₂-SnO₂ Ternary Nanocomposites for High-Performance Asymmetric Supercapacitors. *ACS Omega* 7:43981–43991.
<https://doi.org/10.1021/acsomega.2c05343>
 20. Khuspe GD, Navale ST, Chougule MA, et al (2013) Facile method of synthesis of polyaniline-SnO₂ hybrid nanocomposites: Microstructural, optical and electrical transport properties. *Synth Met* 178:1–9.
<https://doi.org/10.1016/j.synthmet.2013.06.022>
 21. Morawska K, Pietrzak K, Car J, et al (2026) A New Type of Nitrate Potentiometric Sensor Prepared Using Hybrid Metal Oxide/Metal Nanoparticles. *Materials (Basel)* 19:1–20. <https://doi.org/10.3390/ma19050847>
 22. Li Y, Pan Y, Xing Y, et al (2025) High-Reproducibility and -Stability All-Solid-Contact Nitrate Ion-Selective Electrode with CoWSe₂ as Solid Contact for Nitrate Monitoring in Wetland Soil. *ACS Sensors* 10:4162–4171.
<https://doi.org/10.1021/acssensors.5c00274>
 23. Solaiman M, Galib AR, Riam SZ, et al (2025) Real-time potentiometric sensing of soil nitrate: Depth-resolved monitoring across plant species with varying root structures. *Comput Electron Agric* 239:110929.
<https://doi.org/https://doi.org/10.1016/j.compag.2025.110929>
 24. Li Y, Wu J, Zhang H, et al (2023) An all-solid-state ion-selective sensor based on polyaniline for nitrate-nitrogen detection. *J Mater Sci* 58:17292–17302.
<https://doi.org/10.1007/s10853-023-09112-z>
 25. Jiang H, Lai K, Waimin JF, et al (2025) Manufacturing parameter optimization of solid-state nitrate ion-selective sensors and their laboratory and field testing. *Sensors Actuators A Phys* 393:116810.
<https://doi.org/https://doi.org/10.1016/j.sna.2025.116810>
 26. Morawska K, Malinowski S, Krawczyk J, Wardak C (2024) Multi-Walled Carbon Nanotubes and Copper Oxide Nanoparticles Composite Used as Transducer Medias in Nitrate Ion-Selective Electrodes. *J Electrochem Soc* 171:087511.
<https://doi.org/10.1149/1945-7111/ad6b49>
 27. Thuy NTD, Wang X, Zhao G, et al (2022) A Co₃O₄ Nanoparticle-Modified Screen-Printed Electrode Sensor for the Detection of Nitrate Ions in Aquaponic Systems. *Sensors* 22:1–16. <https://doi.org/10.3390/s22249730>
 28. Forrest T, Zdrachek E, Bakker E (2020) Thin Layer Membrane Systems as Rapid Development Tool for Potentiometric Solid Contact Ion-selective Electrodes. *Electroanalysis* 32:799–804. <https://doi.org/https://doi.org/10.1002/elan.201900674>
 29. Zhang Z, Papautsky I (2021) Miniature Ion-selective Electrodes with Mesoporous Carbon Black as Solid Contact. *Electroanalysis* 33:2143–2151.

<https://doi.org/https://doi.org/10.1002/elan.202100088>

30. Onder A, Begar F, Kibris E, et al (2025) Nitrate sensing with molecular cage ionophores: a potentiometric approach. *Sensors and Diagnostics* 4:432–442. <https://doi.org/10.1039/d4sd00359d>
31. Niemiec B, Piech R, Paczosa-Bator B (2023) All-Solid-State Carbon Black Paste Electrodes Modified by Poly(3-octylthiophene-2,5-diyl) and Transition Metal Oxides for Determination of Nitrate Ions. *Molecules* 28:. <https://doi.org/10.3390/molecules28114313>
32. Fayose T, Thomas E, Radu T, et al (2021) Concurrent measurement of nitrate and ammonium in water and soil samples using ion-selective electrodes: Tackling sensitivity and precision issues. *Anal Sci Adv* 2:279–288. <https://doi.org/10.1002/ansa.202000124>
33. Eldeeb MA, Dhamu VN, Paul A, et al (2023) Espial: Electrochemical Soil pH Sensor for In Situ Real-Time Monitoring. *Micromachines* 14:1–11. <https://doi.org/10.3390/mi14122188>