



A comparative study of sol-gel process and chemical precipitation of NiO from fire assay waste: Structural characterization and insights into VOCs sensing application

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ABSTRACT

This study compares nickel oxide (NiO) derived from fire assay waste nickel sulphide (FA-NiS) and chemical precipitation and sol-gel process. This work reports the first time NiO prepared through chemical precipitation from the waste for VOC sensing purposes. Additionally, herein we provide insights into comparing the properties of NiO obtained through different methods and their potential for environmental sensing applications. Structural, morphological, and elemental characterizations are conducted, alongside preliminary investigation into their volatile organic compounds (VOCs) sensing application. After Cu extraction with 5,8-diethyl-7-hydroxydodecan-6-oxime, the nickel (Ni) raffinate was precipitated using lime (Ca(OH)₂) at pH 2.5 and 6.5 conditions. Scanning electron microscope (SEM) -energy dispersive spectroscopy and X-ray photoelectron spectroscopy confirmed nickel and oxygen (O₂) presence at pH 6.5, and iron (Fe), Ni, and O presence at pH 2.5. X-ray diffraction revealed a cubic crystal structure and high average crystallinity (39 - 41 nm) for both sol-gel process and chemical precipitation of NiO. SEM showed uniform, spherical particles for the sol-gel process while chemical precipitation displayed aggregated layered granules. NiO precipitated at pH 2.5 exhibited coalesced hexagonal particles with predominant Fe and Ni presence. Developed analytical methods for inductively coupled plasma optical emission and X-ray fluorescence demonstrated high purity NiO (≈75 %) with low relative standard deviation (RSD <0.05 %) and 90 % recovery using certified reference material. As compared to sol-gel process NiO, the NiO from fire assay waste displayed clear sensing responses at both 25 °C and 150 °C, with recovery times (80 and 120 seconds) even at the lowest concentration (1.5 ppm). The highest response (R_g/R_a = 1.198 for 45 ppm ethanol) occurred at 150 °C, indicating the potential NiO from the fire assay waste as a futuristic device for VOCs sensing under ambient conditions.

1. Introduction

Every year, tons of waste is produced by pyrometallurgical and extractive metallurgical processes during the minerals and ore recovery process (Kalisz et al., 2022), (Matinde et al., 2018). Metals and their oxide wastes are widely available in industries like metal manufacturing, electronics, battery materials, printed circuit board waste (PCBs) (Łukomska et al., 2022), and mineral processing (Meng et al., 2022). The waste contains valuable metals and other toxic compounds, if improperly retrieved, might seriously threaten the environment and if not recycled may contribute to the depletion of natural resources (Matinde et al., 2018). Mining companies are exploring novel

methods to retrieve high-grade nickel (Ni), a coveted base metal. Prolonged exposure to metals like Ni, cobalt (Co), copper (Cu), and others can result in a range of health concerns, including respiratory infections, typhoid fever, lung fibrosis, as well as kidney and cardiovascular disorders (Basturkcü, H et al., 2017). In addition, the demand and prices of commodity and strategic critical minerals are expected to rise due to their importance in various high-technology industries such as electronics, and energy sources (Han et al., 2023). Thus, extensive research on the recovery and precipitation of critical minerals from alternative sources including wastewater streams, fire assay nickel sulphide (NiS) waste and refuse piles (Krishnan et al., 2021).

It is well known that removing Ni is a challenging and hence scien-

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tific task. Numerous treatment methods, including ion exchange on zeolites, chelating resins, adsorption on activated carbon, chemical precipitation, microfiltration, and ion exchange on zeolites, have been proposed for the removal of Ni from aqueous waste streams (Krishnan et al., 2021), (Pohl, 2020), (K. Dermentzis, 2010). Some of these techniques are limited in application to generate a huge amount of sludge which leads to another secondary pollution of the environment and high effluent cost and high energy required (Zinicovscaia et al., 2020). Chemical precipitation using precipitating agents such as lime ($\text{Ca}(\text{OH})_2$) and sulphide is the most economical and widely used method for treating industrial effluents containing heavy metals, although it can lose its effectiveness when significant complexing agents are present (Dermentzis et al., 2016), (Kartal et al., 2023). The chemical precipitation uses an alkaline agent such as $\text{Ca}(\text{OH})_2$ or sodium hydroxide (NaOH) which increases the pH and subsequently decreases the solubility of the metal ion which results in their precipitation in the form of metal hydroxide from solvent in the form of the following general mechanism (Pohl, 2020) in equation 1:



These developments have inspired researchers to play a pivotal role in synthetic and recycling technologies to produce and recover valuable metals and metal oxide. Metal oxides have attracted considerable interest due to their potential application in numerous fields, including electronics, energy conversion, bio-sensing, volatile organic chemicals sensing and energy storage (Altammar, 2023). The base metal oxides such as copper oxide (CuO) and nickel oxide (NiO) are n-type and p-type semiconductors with 1.24 and 2.4 to 3.5 eV band gaps respectively (Singh et al., 2022), (Sabirin et al., 2013). Their intriguing properties such as band gap indicate the potential application for gas sensing, with high sensitivity, and selectivity for VOC sensing. The sensing properties of the Metal Oxide (MeO) depend on the chemisorption of the oxygen species in negative charge (O^{2-} , O^- and O^{-2}) in the air due to charge transfer between the analyte (Oxygen) and MeO surface which depends on oxygen vacancies, electron density and electrical conductivity (Sharma & Kumar, 2024). The key factors influencing the properties of metal oxide that control oxygen vacancies are the synthesis technique, processing, and operating conditions (Al-hashem et al., 2019), (Katoch et al., 2013). There are several methods reported in the literature for the fabrication of metal oxides and recovery of these metals from waste such as waste PCBs (Chavali et al., 2019) by optimizing temperature conditions and the type of solvent used during extraction. The precipitation approach is one of the best ways to prepare metal oxides out of all of these synthetic processes. Compared to other ways, the precipitation method is the most straightforward and least expensive way to grow metal oxides at low temperatures while maintaining size control (Mala et al., 2023). In addition, recovery methods for metals and their oxide include extractive metallurgy and pyrometallurgical methods which utilise the long-chain polymeric solvent and high-temperature furnace respectively. Among the preparation methods for metal oxides (MOs), the sol-gel process has attracted considerable attention due to its ease of preparation, high degree of homogeneity, low cost and the possibility of forming small particles at room temperature (Parashar et al., 2020). Other advantages of MOs form a chemiresistive phenomenon with metal oxide-based sensors where oxygen molecules are adsorbed on MO's surface to form a hole-electron accumulation (Goel et al., 2023). The extensive search on synthetic processes and recovery of MO from waste for re-purpose and to cushion the environment issues by removal of toxic metal in the waste streams and sensing of toxic gases.

Herein, we compare the NiO extracted and precipitated from fire essay (NiS) waste and NiO prepared from the sol-gel process as a reference for chemical properties. To the best of the author's knowledge, there is no study reported on the recovery process of NiO from fire essay waste for re-use, purpose in VOC sensing. Herein, we report the recovery and precipitation of NiO from PGM collector (NiS) waste and compare it

to sol-gel prepared NiO . The elemental, statistical analysis, and structural characterization employed are ICP-OES, XRF, and analysis of variance (ANOVA) tool, XRD, SEM-EDS, FTIR and XPS. In addition, the preliminary analysis of NiO towards VOCs sensing application towards ethanol was conducted.

2. Experimental details

2.1. Materials and reagents

In this method, the following chemicals and reagents that were used for the experiment, are Nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2$) obtained from Sigma Aldrich (South Africa), ethanol (EtOH) 99.9 % (Merck), nitric acid 65 % (w/w) from Merck, Acetic acid (CH_3COOH) (Merck), sodium hydroxide (NaOH), and Hydrochloric acid (Merck), 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) supplied by BASF was used. NiS waste was collected from the Analytical Chemistry Laboratory at Mintek in Randburg South Africa. All reagents were analytical grade and were used without further modification. Throughout the studies, the Milli-Q system Type 1 water (Merck) was used to prepare ultrapure water (18.2 M Ω cm).

2.2. Preparation methods

2.2.1. Sol-gel process

NiO was synthesized using a sol-gel process by mixing 0.5 g of $\text{Ni}(\text{CH}_3\text{COO})_2$ and 40 mL of EtOH in a 200 mL beaker. The solution was stirred using the magnetic stirrer bar for 1h and the viscous green solution was formed. Thereafter, 1M hydrochloric acid (HCl) was added dropwise and the solution was stirred, and then the temperature was adjusted to 60 °C and the gel was formed. After 2h, the gel was heated to 100 °C for 1h and the crystals formed were crushed using mortar and piston. The green powder was calcined for 3h at 350 °C. Fig 1 summarizes the synthetic route and step-wise of the sol-gel process.

2.2.2. Solvent extracted and selective precipitation of NiO

As summarized in the schematic in Fig 2, the NiS waste was added in 250 mL as a pregnant leach solution (PLS). The PLS was stirred for 30 min. Then, the solution was added in a 500 mL separating funnel, then a 1:5 ratio of the extracting solvent 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) was added and the solution was shaken gently to form a loaded organic ($\text{Org}_{\text{Loaded}}$). The $\text{Org}_{\text{Loaded}}$ and aqueous solution was separated and the Ni- raffinate settled at the bottom and was collected in the aqueous solution as explained in literature Mabowa et al. (2024). Thereafter, lime $\text{Ca}(\text{OH})_2$ was introduced to the Ni- raffinate for the chemical precipitation process. The pH was adjusted to 2.5 and 6.5 to precipitate $\text{Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ respectively.

2.3. Characterization

This work used the following high-resolution instrumentation and advanced analytical techniques to examine the structure, morphology and elemental composition. Fourier-transform infrared spectroscopy (FTIR), Bruker vertex 70 technique was used to analyse the bond stretching frequencies of NiO -based compounds. The structure and crystallinity phase of NiO -based materials were determined using powder X-ray diffraction (XRD, Bruker D8 advance diffractometer, Cu_K radiation, $\lambda = 1.54060\text{\AA}$, operated at 20 kV and 40 mA). The patterns were obtained at 2θ between 10-90° at 2°min^{-1} . Field emission scanning electron microscopy (FE-SEM) was performed using JEOL JSM-7800F with an EDX detector for elemental composition. X-ray photoelectron spectroscopy (XPS), elemental composition or metal concentration is determined using Agilent 5510 Vertical dual view (VDV) ICP-OES, and HITACHI, XRF analyser (x-met 8000 expert Geo).

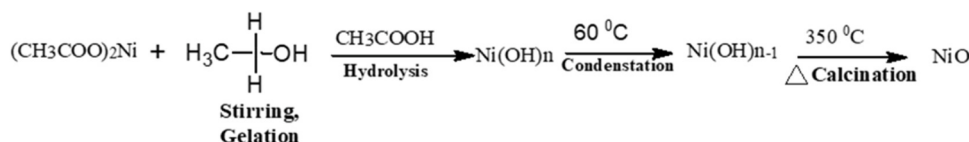
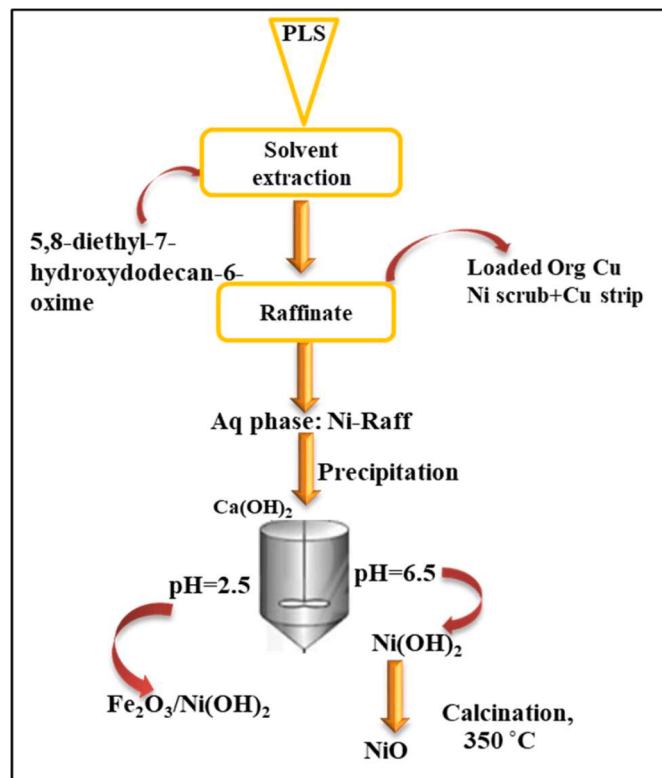


Fig. 1. Schematic synthetic route of sol-gel process of NiO

Fig. 2. Schematic diagram showing solvent extraction and chemical precipitation $\text{Ni}(\text{OH})_2$ and $\text{Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2$

3. Results and discussion

Fig. 3 (a), and 3(b) illustrate the FTIR spectrum of NiO prepared through chemical precipitation, and sol-gel process respectively, indicating calcined chemical precipitation NiO. In all the FTIR spectra, there is a prominent and broad peak around 3400 cm^{-1} that is attributed to $\nu(\text{OH})$ asymmetric stretching vibration which is the characteristic feature of $\beta\text{-Ni}(\text{OH})_2$ (Qin et al., 2020) (Mala, Nazir Ahmad, S, Sivakumar, 2021) formed before the calcination process. The spectral peak around $550\text{--}620\text{ cm}^{-1}$ is assigned to $\nu(\text{NiO})$ stretching mode. The vibration peak observed around 1422 cm^{-1} and 1622 cm^{-1} is assigned to $\delta(\text{OH})$ bending vibration and stretching of carboxylic νCO_3^{2-} stretching respectively (Singh et al., 2022) (Qin et al., 2020). The transformation of $\beta\text{-Ni}(\text{OH})_2$ to NiO through calcination is confirmed by the drastic peak intensity reduction around 3400 cm^{-1} . There is a prominent wave number shift from 3400 cm^{-1} ($\text{Ni}(\text{OH})_2$) to 2969 cm^{-1} of NiO (insert) that indicates the transformation of functional group. Furthermore, the lack of $\delta(\text{OH})$ bending mode around 1622 cm^{-1} from water is attributed to high NiO crystalline, with less water held by hydrogen bonding (Mabowa et al., 2024). Noteworthy, the stretching vibration for calcined NiO shifted to a higher wave number (from 630 to 786 cm^{-1}) which indicates the phase ($\text{Ni}(\text{OH})_2$) to NiO transformation. Likewise, NiO from sol-gel was prepared to exhibit similar results as calcined NiO. The results indicate that $\text{Ni}(\text{OH})_2$ was precipitated from the waste and further calcined, similar to the sol-gel process the FTIR spectrum

exhibits the typical NiO. The later results strongly agree with the literature (Fazlali et al., 2019).

In Fig. 3 (c-d), XRD represents the NiO precipitated from the sol-gel process and chemical precipitation. The transformation of $\text{Ni}(\text{OH})_2$ to NiO was observed upon the calcination process at 350°C . Evidently, the diffraction peaks depict the $\beta\text{-Ni}(\text{OH})_2$ formed during the precipitation process. All diffraction peaks for room temperature chemical precipitation $\text{Ni}(\text{OH})_2$ confirms the $\beta\text{-Ni}(\text{OH})_2$ hexagonal phase and the peaks indexed 2θ values 24°C , 29°C , 30°C , 45°C , 50°C , and 60°C corresponding to (001), (100), (101), (102), (103), (110) respectively which is in agreement with the literature (Qin et al., 2020), (Thimmasandra Narayan, 2015). The results indicate that crystalline NiOx was precipitated successfully. Furthermore, for the un-calcined sol-gel process NiO indicates the amorphous phase. Both calcined sol-gel process NiO and chemical precipitation exhibit a similar XRD pattern indexed at 35° , 44° , 65° , 75° , and 80° corresponding to (111), (200), (220), (311) and (222) planes, respectively which is attributed to NiO cubic crystal structure and matches with the Joint Committee on Powder Diffraction (JCPDSO: #73-1520) standard. In addition, XRD results are in strong agreement with FTIR results (Fig. 3). Using the Debye-Scherrer equation as described in literature (Etape et al., 2017), chemical precipitated NiO exhibited higher crystalline size (41.1 nm) as compared to sol-gel process (38.5 nm). The results are summarized in table S4 (supporting information).

X-ray photoelectron spectroscopy (XPS) analysis was used to characterize the electron surface of NiO. Fig 4 (a) depicts the NiO spectra survey which displays the prominent peak around 880 eV , 540 eV and 250 eV binding energy, corresponding to Ni2p, O1s and C1s respectively. The results confirm the high purity of NiO with low impurity as indicated by low carbonaceous peak (C1s). Fig 4 (b) displays the spectrum of Ni2p with doublet peaks situated at 860 eV and 880 eV binding energy which are attributed to Ni2p ($2/3$) and Ni2p ($1/2$) respectively. The higher O1s for metal oxide in Fig 4 (c) than O1s of carbonaceous peak confirms the strong bond between Ni and oxygen and indicates the purity of NiO. Likewise, in Fig 4 (d-f) the XPS spectra survey chemical precipitated NiO exhibit a similar chemical composition, except for the Calcium (Ca) and Chloride (Cl) impurities. These impurities are due to the HCl matrix of fire assay waste and Ca from the $\text{Ca}(\text{OH})_2$ neutralizing agent. The are two prominent peaks around 858 and 873 eV separated by its satellite around 862 eV , which correspond to Ni2p($3/2$), and Ni2p ($1/2$) respectively. The later results confirms the presence of NiO (Huang et al., 2017). The prominent O1s peak indicates high oxygen vacancies which could be MO with enhanced gas-sensing properties. Furthermore, the chemical oxidation states of the as-prepared NiO are summarized in table S2 (supplementary information).

SEM and EDS were used to examine the surface morphology and to profile the elements of chemical precipitation at different pH (2.5 and 6.5) and compare them to NiO prepared via sol-gel process. Fig 5 (a-c) represents the SEM image of NiO at pH 6.5 25°C and 350°C . As discussed by this group in the literature (Mabowa et al., 2024), Fig (5a) revealed the rough and agglomerated $\text{Ni}(\text{OH})_2$ particles which are in agreement with the literature (Zunaidi et al., 2022). Whereas Fig 5 (b) exhibits the flat surface and reduced particle size. These later results are due to the loss of water and other impurities during the calcination at 350°C . In contrast to chemical precipitation, the NiO sol-gel prepared shows round particles in Fig 5 (c) that are aggregated. The results are ascribed to the typical sol-gel process of metal oxide (Kessler & Seisenbaeva, 2023), (Arya et al., 2021). Fig. 5 (d) illustrates the

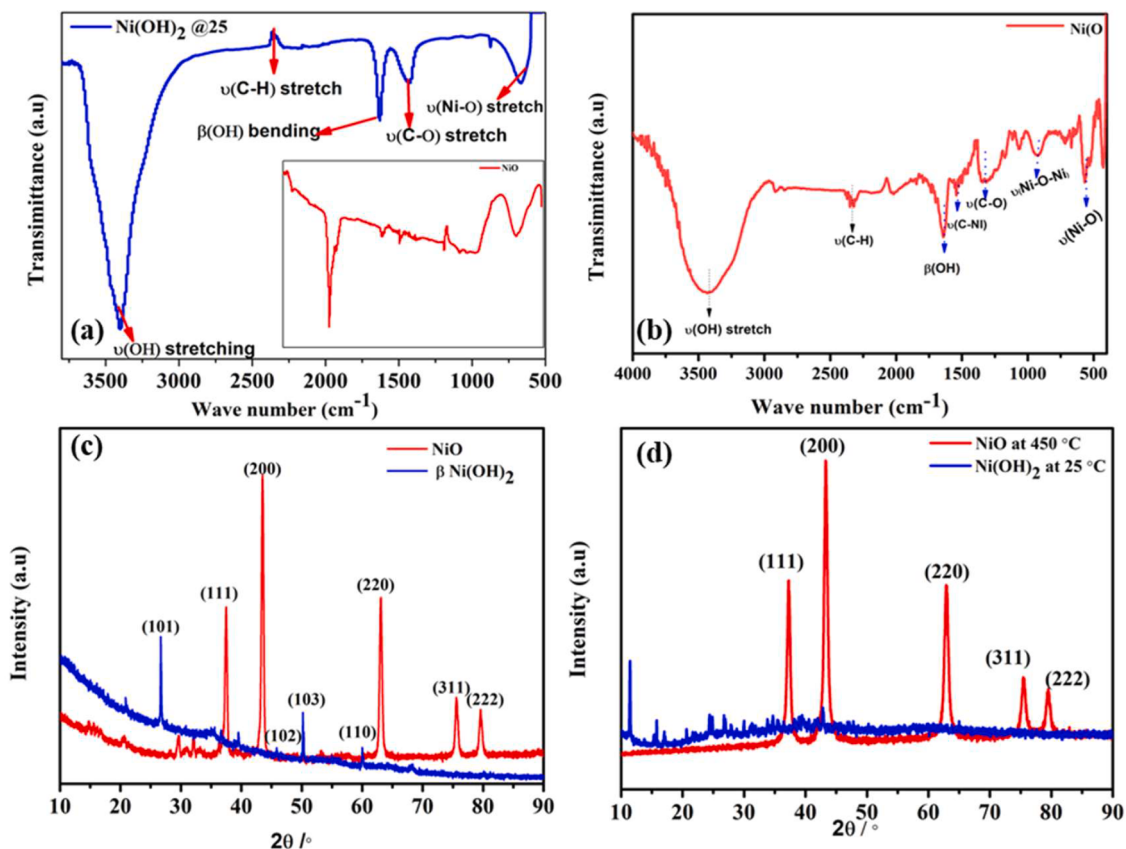


Fig. 3. FTIR spectrum of NiO from chemical precipitation (a) and sol-gel process (b), XRD pattern of chemical precipitation NiO (c), and (d). sol-gel process NiO

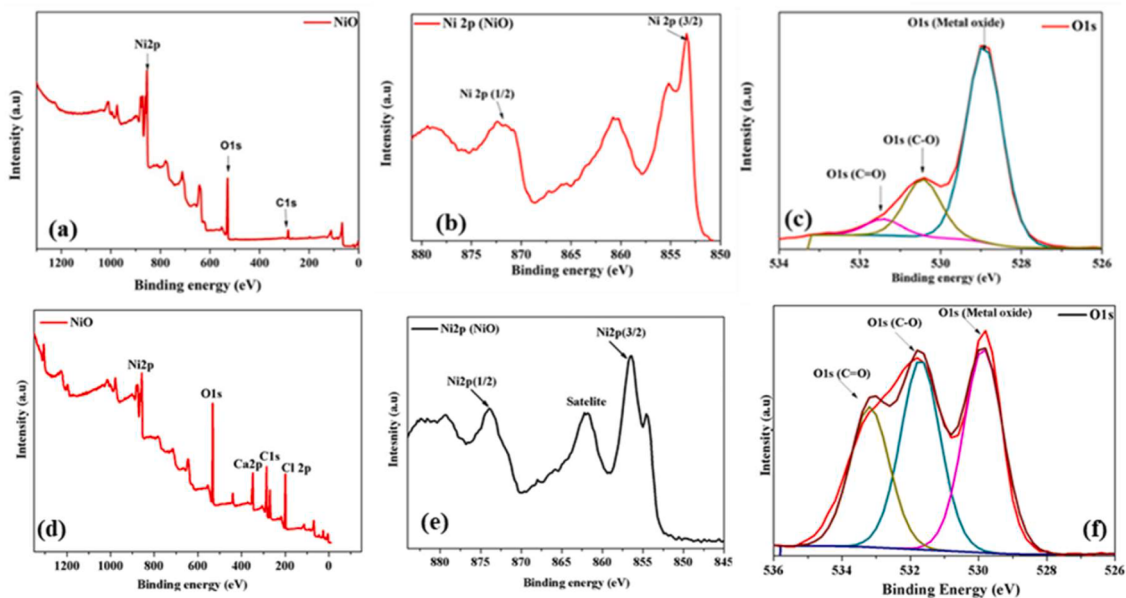


Fig. 4. XPS spectra survey, Ni2p and deconvoluted O1s of sol-gel process NiO (a-c) and of chemical precipitated NiO (d-f).

precipitation of $\text{Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2$ at 6.5 as described by this group in previous studies (Mabowa et al., 2024), showing layered rough granules which typical goethite ($\alpha\text{-FeOOH}$) which corroborated with the literature (Satyananda et al., 2017). However, the calcination process liberated the typical hexagonal $\alpha\text{-Fe}_2\text{O}_3$ particle shape in strong agreement with literature (Woo et al., 2019), (Lin et al., 2014). The shape confirms the improved crystallinity of Fe_2O_3 after the loss of carbonaceous and

H_2O impurities. Fig 5 (c) displays the EDS which indicates the existence of Ni and O. The high Ca is attributed to $\text{Ca}(\text{OH})_2$ utilised for precipitation. In comparison to the sol-gel process, NiO reveals the existence of Ni and O at high purity as displayed in Fig 5 (f). Fig 5 (i) indicates the significant loss of Ni and dominance of Fe at pH 2.5, the loss is discussed in literature (Wang et al., 2011). The later results confirm the loss of Ni at pH above 4 in goethite. The EDS spectra lines have improved the

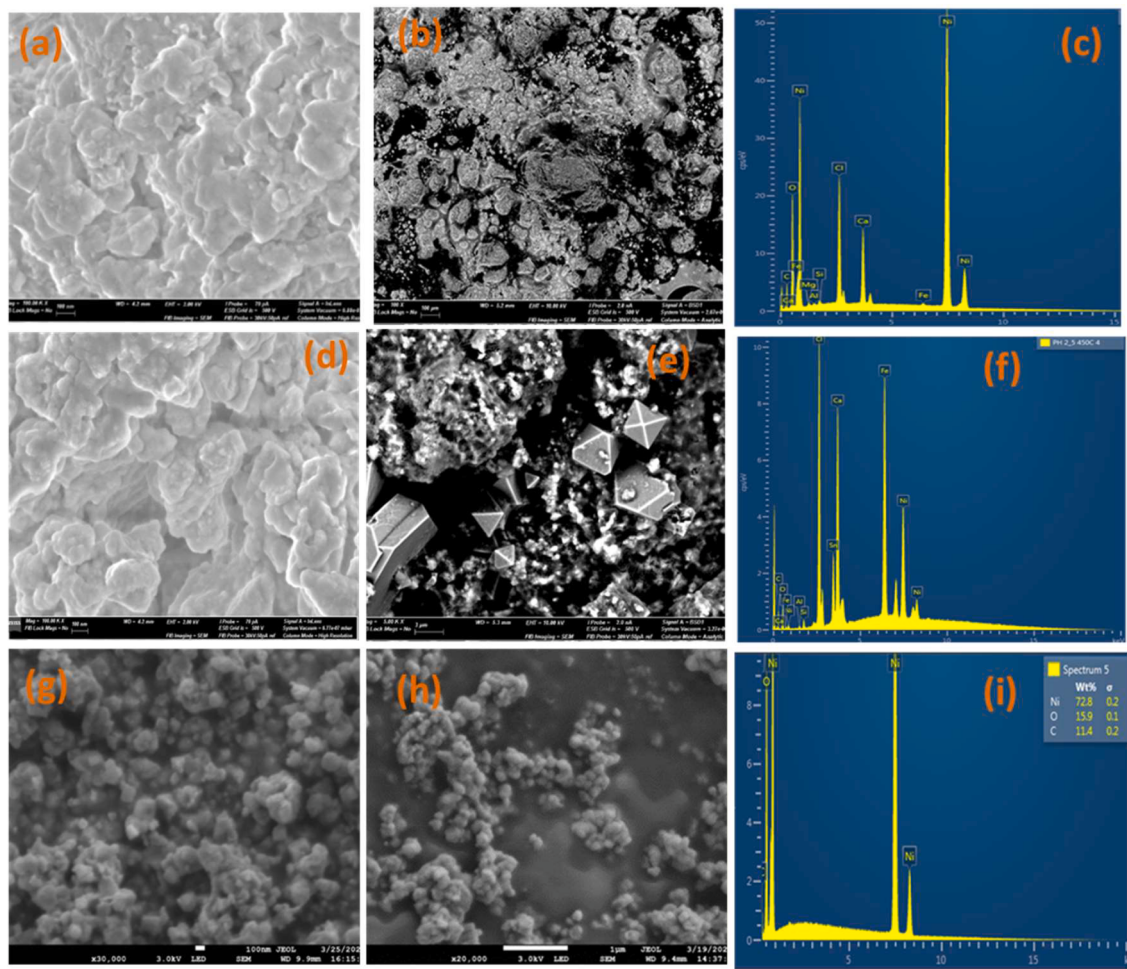


Fig. 5. (a-c) SEM micrograph and EDX of NiO from chemical precipitation at pH 6.5 and (d-f) chemical precipitation at pH 2.5 (g-i) and sol-gel process NiO

intensity for the calcined precipitate at pH 6.5 and pH 2.5 as compared to un-calcined materials displayed in Fig S1 and Fig S2 (supplementary information). The latter results indicate improved crystallinity and less impurity.

The ICP-OES analysis was employed to determine the concentration of major elements such as Ni, Fe, Co, and Cu to name a few to profile the Fe and Ni loss and recovery from PLS, raffinate and the precipitated material at different pH conditions. The results for elemental concentration are summarized in [table 2](#). For precipitated samples, alkaline fusion was used followed by acid digestion using hydrochloric acid (HCl) as described in literature ([Uchida et al., 2005](#)), with slight changes. Whereas the liquid sample from raffinate was digested using HCl. Before analysis, the instrument was calibrated using the multi-element 1000 ppm stock solution. The known concentration solutions were used as quality control systems (QCs) and certified reference materials (CRM); AMIS 56 and 51/71 were also analysed for quality control. It was observed that the Ni concentration was increased when the pH is adjusted to 6.5 and there is significant Ni loss when the pH decreases which is consistent with EDS ([Fig 5](#)). While the pH decreases up to 2.5 during precipitation, Fe content increases which promotes the mixture of Ni and goethite (α -FeOOH) precipitation as described in literature ([BASTURKCU & Acarkan, 2017](#)). The findings are consistent with XRF results in [table S3](#) (supplementary information) and EDS results ([Fig 5](#)). As observed in [table 1](#), there is a significant drop of Cu from the head solution (PLS), to raffinate (3.87 ppm to 0.81ppm) which corresponds to Cu-loaded organic (Cu-LIX 63-70). This is due to coordinating of Cu with the nitrogen atom of the oxime group as indicated by [Fig 1](#) and expressed in the following [equation 2](#) ([Shakibania et al., 2020](#)), ([Elizalde et al.,](#)

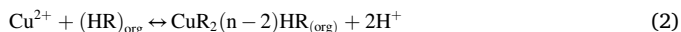
Table 1
Summary of Ni(OH)₂ and NiO functional groups

Functional group	Wave number (cm ⁻¹)	Assignment
ν (NiO)	550-620	Stretching mode of O-Ni-O
β (-OH)	1422	OH bending of Ni(OH) ₂
ν C-O,	1622	Stretching vibration of carboxylic species
ν (OH)	3400	Asymmetric OH stretch vibration of H ₂ O
ν (C-H)	2800	Stretch vibration of carbon species

Table 2
ICP-OES results for major elements.

Materials	Elements		
	Ni (%)	Fe(%)	Cu(%)
PLS	62.3	4.72	3.87
SX Ni-raffinate	50.29	2.58	0.81
Precipitate pH 2.5	6.08	7.12	3.4
Precipitate pH 6.5	28.24	0.12	0.17
CRM: amis56	0.196	7.008	0.151
Accurate value	0.2	7.02	0.14
SARM 33	0.21	55.34	0.23
Accurate value	0.27	-	0.26
	0.28	-	0.29

2019).



The XRF analysis was used to examine the elemental composition of the precipitate at different pH (2.5 and 6.5). As illustrated in table S3 (supplementary information), all samples including the certified reference material (CRM; AMIS 56 and 51/71) were analysed in duplicate and expressed in two decimals. The results from XRF show the consistency with EDS results displayed in Fig 5. It was observed that the sol-gel process NiO indicates the highest Ni and O content which confirms the formation of NiO. Furthermore, chemical precipitation NiO precipitated at acidic conditions (pH 2.5) exhibited a slight decrease of Ni from and higher Fe₂O₃. The results are comparable with the findings from α -FeOOH precipitation in an acidic environment as explained in the literature (Davey & Scott, 1976), (BASTURKCU & Acarkan, 2017).

4. Sensing application

Before the sensing experiment was resumed, the gas flow test was conducted at different temperatures as displayed in Fig S5 (supplementary information). In Fig 6(a-d) and table S4 (supplementary information), NiO showed an increase and clear linear response up 1.198 of ethanol gas concentration ranging from 1.5ppm to 45 ppm. Interestingly, the NiO sensing type indicates the transformation of p-type NiO to n-type NiO as depicted in Fig S6 (supplementary information) which could be due to the adsorption of oxygen species (O_2^-) of ethanol with NiO, creating a higher electron density upon the electron-hole accumulation as explained in literature (Nkosi, S.S, Mkwae et al., 2022). Additionally, the NiO shows the sensing ability at room temperature, however with a higher response. As indicated in Fig 6, the resistance increases with increase in temperature from 25 °C to 250 °C. The

increase in resistance is attributed to the decline of NiO hole upon the chemisorption of oxygen species (O_2^- (ads) and O^- (ads) which they donate the electron back to NiO's conduction band. As illustrated in table S4 (supplementary information) and Fig 7, the response decreases at higher temperatures (250 °C). However, the higher response is observed at 150 °C. As shown in Fig 7 (a-d), in all concentration value, 150 °C reveal the higher response, which is ascribed to more O_2 electrons captured by the conduction band of NiO. Furthermore, NiO reveals a higher response at higher concentration as displayed in Fig 7.

4.1. NiO fundamental gas sensing mechanism

The ethanol sensitivity of the NiO predominantly depended on the gas adsorption on the NiO surface. NiO is the p-type semiconductor, however, according to the above response exhibits the n-type gas sensing properties. When NiO material is placed in the air, the O_2 molecule is adsorbed on the surface and forms O_2 species (O_2^- , O^- , O^{2-}) ions through trapping electrons (e^- s by O_2 from the conduction band of NiO, were filled the electron density which recombined with the hole and decreasing the hole. It was observed that resistance increased and current increased. Since electrons make up the majority of MOSS' charge carriers, exposure to reducing gas (Ethanol) causes n-type Metal oxide conductance to increase. When ethanol is exhausted the O_2 gas molecules get re-adsorbed to the surface of the materials. The general mechanism can be expressed by different equations 3-7;

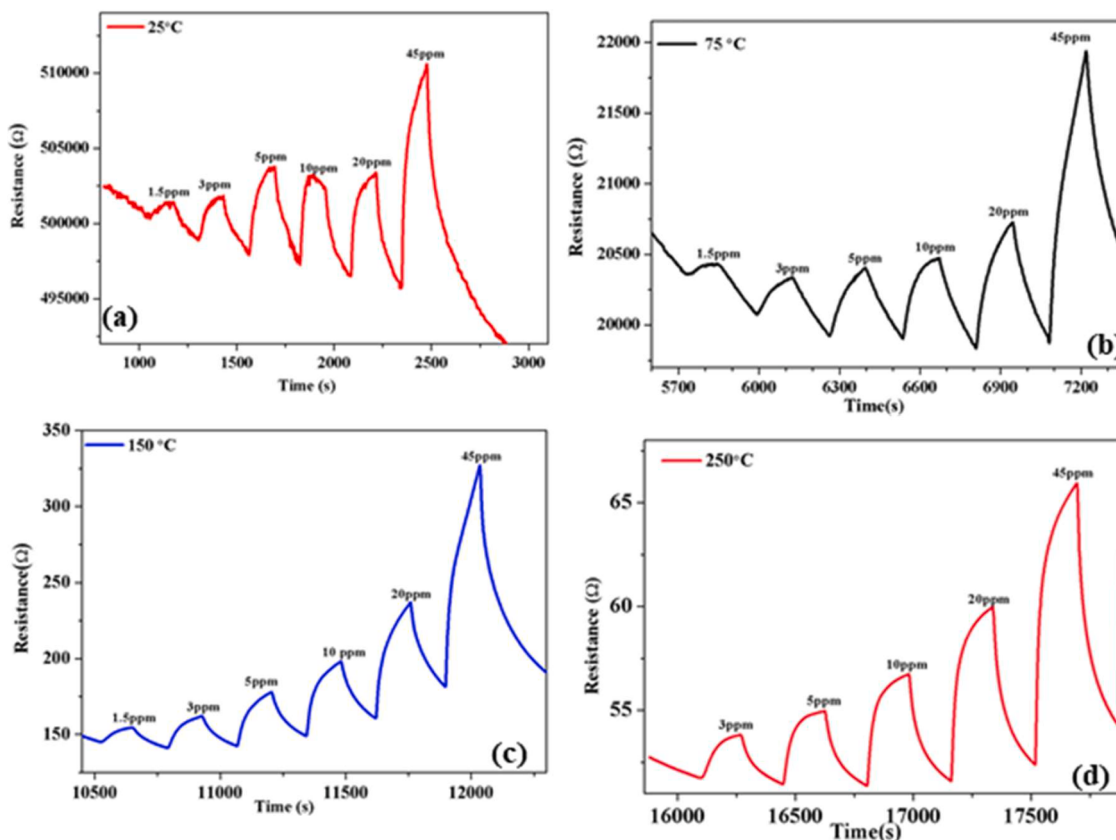


Fig. 6. Sensing resistance of nickel oxide towards ethanol, exposed in various time intervals at different concentrations (1.5 ppm, 3 ppm, 5 ppm, 10 ppm, 20 ppm, 45 ppm) at 25 °C, 75 °C and 150 °C and 250 °C.

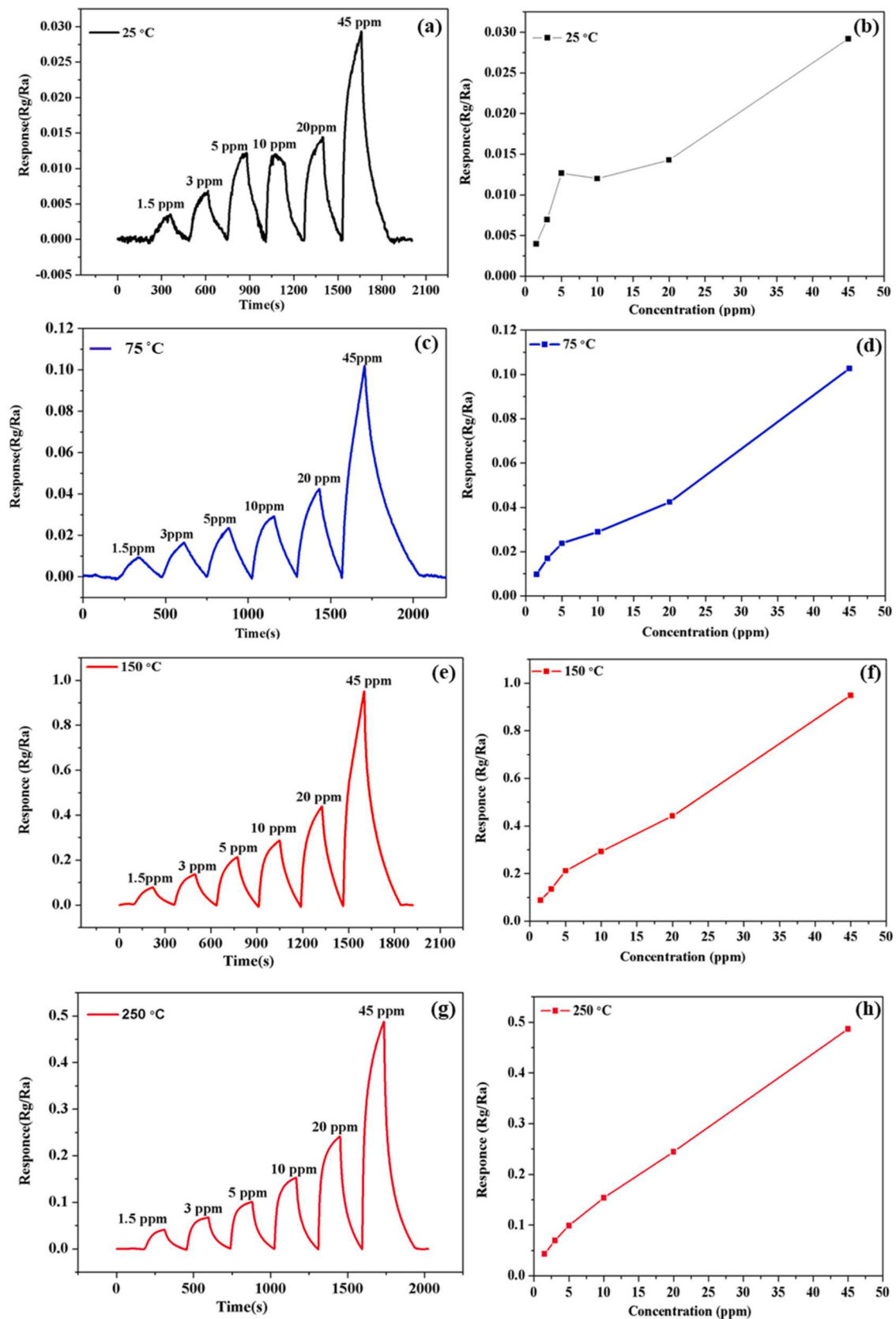
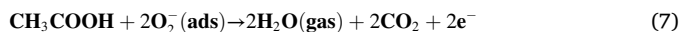


Fig. 7. Sensing response of NiO towards ethanol at different exposure times at various concentrations (1.5 ppm, 3 ppm, 5 ppm, 10 ppm, 20 ppm, 45 ppm) (a-b) at 25 °C, (c-d) 75, (e-f) 150 °C and (g-h) at 250 °C.



Additionally, when the examined polar volatile organic compounds (VOCs) are adsorbed on reduced surfaces, there is very little interaction between the pre-adsorbed oxygen species and the VOCs. Because the free electrons are trapped, a surface electron depletion layer is formed, which lowers the NiO conductivity and carrier concentration (Ahmed A. Abokifa, Kelsey Haddad, John Fortner, Cynthia S. Lo, 2017).

CRediT authorship contribution statement

Happy Mothepane Mabowa: Writing – review & editing, Writing – original draft, Investigation, Conceptualization. **Andile Mkhohlakai:** Writing – original draft, Methodology, Formal analysis, Data curation. **Luke Chimuka:** Writing – review & editing, Supervision, Resources. **James Tshilongo:** Writing – review & editing, Supervision, Funding acquisition, Data curation.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Conclusion

Sol-gel process of NiO and recovery of NiO from NiS waste was done successfully. 5,8-diethyl-7-hydroxydodecan-6-oxime reveals high efficiency in liberating Ni to the aqueous raffinate phase while efficiently loading the Cu in the organic phase. Ni(OH)₂ and Fe₂O₃/Ni(OH)₂ were precipitating agents, Ca(OH)₂ at pH 6.5 and 2.5 respectively as confirmed by physicochemical characterization and elemental analysis. The predominance of Ni, O at pH 6.5 enhances the sensing performance of NiO. The calcination process removed the impurity and improved the crystallinity. The elements analysis using ICP-OES and XRF are in strong agreement with the S-curve precipitation, exhibiting the loss of Ni at lower pH. The results 5,8-diethyl-7-hydroxydodecan-6-oxime and Ca(OH)₂ are classical and efficient reagents to remove toxic and critical elements from waste streams. In addition, the reference NiO exhibits detected ethanol at room temperature with a clear response at low concentrations. These findings highlight the potential of NiO as a futuristic device for sensing the VOC at ambient conditions. The results indicate the extracted NiO from NiS waste shows the potential for sensing VOCs, because of the intriguing properties. Recycling and repurposing of NiS waste have a high potential of realizing critical minerals and mitigating the environment while contributing to a circular economy.

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Supplementary information

The utilisation of the advanced analytical techniques and high-resolution instrument are essential for evaluating the effectiveness of

the solvent extraction pre-treatment in mitigating Cu loss during precipitation to understand the composition and structure of the precipitated material. The supplementary information provided in fig S1, S2, S3 and S4, S5, S6 in support of the comprehensive analysis of the surface morphology and elemental composition of the sample by EDX, XPS analysis, gas flow and response as function of time.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envadv.2024.100531.

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