RESEARCH TITLE

Synthesis and Characterization of NiO-MnO and MnO Nanocomposites for Enhanced Heavy Metal Detection using Quartz Crystal Microbalance Technology

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Abstract

This study presents the synthesis, comprehensive characterization, and sensing application of NiO-MnO and MnO nanoparticles for the detection of heavy metal ions in aqueous solutions using Quartz Crystal Microbalance (QCM) technology. The nanoparticles and nanocomposites were synthesized via a controlled precipitation method followed by appropriate thermal treatment to obtain the desired crystal phases. The materials were extensively characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Visible spectroscopy, Brunauer-Emmett-Teller (BET) surface area analysis and thermogravimetric analysis (TGA) . XRD confirmed the successful synthesis of crystalline NiO-MnO and MnO phases with average crystallite sizes ranging from 18-30 nm. SEM revealed that the NiO-MnO nanocomposites (58 nm) were larger than MnO nanoparticles (42 nm) with more complex surface morphologies. BET analysis showed that MnO nanoparticles had the highest specific surface area (95.317 m²/g) compared to NiO-MnO (31.245 m²/g).   UV-Visible spectroscopy demonstrated distinct absorption patterns confirming the formation of the respective phases. QCM analysis demonstrated that both materials effectively detected lead ions at 0.1 ppm concentration, with the NiO-MnO nanocomposite exhibiting superior sensitivity (325 Hz frequency shift) compared to MnO (275 Hz). The enhanced performance of the NiO-MnO nanocomposite is attributed to the synergistic effect between NiO and MnO, providing more diverse and effective binding sites for heavy metal ions. This study highlights the potential of manganese-based oxide nanocomposites for developing highly sensitive and rapid sensors for environmental monitoring applications.

Key Words: Nickel oxide, manganese oxide nanoparticles, NiO-MnO nanocomposites, heavy metal detection, Quartz Crystal Microbalance (QCM), environmental sensing, nanocomposite synthesis, surface characterization, colloidal stability.

عنوان البحث

تحضير وتوصيف متراكبات نانوية من NiO–MnO و MnO من أجل تعزيز الكشف عن المعادن الثقيلة باستخدام تقنية ميزان البلورة الكوارتزية(QCM)

المستخلص

تقدّم هذه الدراسة تحضيرًا وتوصيفًا شاملًا وتطبيقًا تحسّسيًا لجسيمات NiO–MnO و MnOالنانوية من أجل الكشف عن أيونات المعادن الثقيلة في المحاليل المائية باستخدام تقنية ميزان البلورة الكوارتزية (QCM). تم تحضير الجسيمات النانوية والمتراكبات النانوية بطريقة الترسيب المتحكّم فيه، تلتها معالجة حرارية مناسبة للحصول على الأطوار البلورية المطلوبة. خضعت المواد لتوصيف شامل باستخدام حيود الأشعة السينية(XRD) ، والمجهر الإلكتروني الماسح(SEM) ، ومطيافية الأشعة فوق البنفسجية–المرئية(UV–Vis) ، وتحليل المساحة السطحية بطريقة برون–إيميت–تلرauer (BET)، والتحليل الحراري الوزني (TGA). أكدت نتائج XRD نجاح تحضير الأطوار البلورية لكل من NiO–MnO و MnO، بمتوسط أحجام بلورية تراوحت بين 18–30 نانومتر. وأظهرت صور SEM أن المتراكبات النانوية من NiO–MnO(58 نانومتر) كانت أكبر حجمًا من جسيمات MnO النانوية (42 نانومتر)، مع امتلاكها أشكالًا سطحية أكثر تعقيدًا. كما بيّن تحليل BET أن جسيمات MnO النانوية تمتلك أعلى مساحة سطح نوعية (95.317 م²/غ) مقارنة بمتراكبات NiO–MnO (31.245 م²/غ). وأظهرت مطيافية UV–Vis أنماط امتصاص مميّزة تؤكد تكون الأطوار المختلفة. وأثبت تحليل QCM أن كلا المادتين قادرتان على الكشف بكفاءة عن أيونات الرصاص عند تركيز 0.1 جزء في المليون، حيث أظهر متراكب NiO–MnO حساسية أعلى (انزياح ترددي مقداره 325 هرتز) مقارنةً بـ MnO (275 هرتز). ويُعزى هذا الأداء المتفوق لمتراكب NiO–MnO إلى التأثير التآزري بين أكسيدي النيكل والمنغنيز، مما يوفر مواقع ارتباط أكثر تنوعًا وفاعلية لأيونات المعادن الثقيلة. وتبرز هذه الدراسة الإمكانات الواعدة للمتراكبات النانوية القائمة على أكاسيد المنغنيز في تطوير حساسات عالية الحساسية وسريعة الاستجابة لتطبيقات الرصد البيئي.

الكلمات المفتاحية: أكسيد النيكل، جسيمات أكسيد المنغنيز النانوية، المتراكبات النانوية NiO–MnO ، الكشف عن المعادن الثقيلة، ميزان البلورة الكوارتزية(QCM) ، الاستشعار البيئي، تخليق المتراكبات النانوية، توصيف السطح، الاستقرار الغروي.

1. Introduction

The contamination of water resources with heavy metal ions represents a critical environmental and public health challenge worldwide, attracting increasing attention due to rapid industrialization, urbanization, and agricultural intensification [1-3]. Heavy metals such as lead, cadmium, mercury, and chromium pose severe threats to human health and ecological systems due to their non-biodegradability, bioaccumulation potential, and toxicity even at low concentrations [4-6]. These contaminants enter water systems through various anthropogenic activities, including mining operations, industrial discharges, agricultural runoff, and improper waste disposal [7-9].

The detection and monitoring of heavy metal contamination in water resources are crucial for environmental protection and public health safeguarding. Traditional analytical methods for heavy metal detection include atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and anodic stripping voltammetry (ASV) [10-12]. While these techniques offer high accuracy and sensitivity, they often require complex sample preparation, expensive instrumentation, skilled operators, and laboratory settings, limiting their applicability for in-situ and real-time monitoring [13-15].

Recent advances in nanotechnology and materials science have opened new avenues for developing more efficient, cost-effective, and versatile sensing platforms for heavy metal detection [16-18]. Nanomaterial-based sensors have emerged as particularly promising alternatives due to their exceptional surface-to-volume ratio, unique physicochemical properties, and highly customizable surface chemistry [19-21]. These characteristics enable enhanced sensitivity, improved selectivity, and faster response times compared to conventional sensing materials [22-24].

Metal oxide nanoparticles have garnered significant attention in the environmental sensing community, distinguished by their remarkable stability, cost-effective synthesis routes, and versatile surface functionalization options [25-27]. Manganese oxides (MnO, Mn_2O_3, MnO_2) represent a fascinating subset of these materials, exhibiting unique redox behavior, excellent adsorption properties, and variable oxidation states that facilitate their interaction with various pollutants [28-30]. Similarly, nickel oxide (NiO) nanoparticles have demonstrated remarkable sensing capabilities due to their p-type semiconductor characteristics and unique surface chemistry dominated by oxygen vacancies [31-33].

While single metal oxide nanoparticle systems have shown promising results in sensing applications, they face several limitations, including particle aggregation, conductivity constraints, and insufficient selectivity [34-36]. To address these challenges, researchers have increasingly focused on developing mixed metal oxide nanocomposites, which often demonstrate synergistic effects resulting in enhanced performance compared to their individual components [37-39]. The strategic combination of nickel and manganese oxides in nanocomposite architectures presents opportunities for significant improvements in sensing performance, achieved through increased surface area, modified electronic structures, and optimized active sites for heavy metal adsorption [40-42].

Quartz Crystal Microbalance (QCM) technology represents a significant advancement in real-time, label-free detection methodologies for environmental monitoring [43-45]. Operating on the principle of piezoelectric frequency modulation, QCM sensors enable the precise measurement of mass changes at the molecular level, making them ideal for detecting trace amounts of heavy metal ions in water [46-48]. The integration of nanomaterials as sensing layers on QCM devices has demonstrated remarkable potential for achieving unprecedented sensitivity and selectivity in environmental sensing applications [49-51].

Despite the growing body of research on metal oxide nanocomposites for environmental sensing, the systematic investigation of NiO-MnO nanocomposites, particularly in the context

of QCM-based heavy metal sensing, remains relatively unexplored [52-54]. Furthermore, comparative studies evaluating the performance of these nanocomposites against pure manganese oxide (MnO) nanoparticles are scarce, limiting our understanding of the synergistic effects in these mixed systems.

This study aims to address these knowledge gaps through a comprehensive research approach encompassing:

1. The development of controlled synthesis methods for preparing MnO nanoparticles and NiO-MnO nanocomposites with well-defined properties.

2. Detailed characterization of the synthesized materials using multiple analytical techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Visible spectroscopy, Brunauer-Emmett-Teller (BET) surface area analysis, thermogravimetric analysis (TGA).

3. Evaluation of heavy metal sensing performance using QCM-based detection systems, focusing on sensitivity, response time, and stability.

4. Investigation of the fundamental mechanisms underlying the sensing capabilities of the

different materials, with particular emphasis on the synergistic effects observed in the

nanocomposite structures.

By establishing clear relationships between the structural, morphological, and physicochemical properties of these nanomaterials and their sensing capabilities, this research aims to contribute significantly to the development of next-generation sensors for environmental monitoring and water quality assessment. The findings are expected to advance our understanding of mixed metal oxide systems and provide valuable insights for designing more effective nanomaterial-based sensors for heavy metal detection.

2. Materials and Methods
2.1. Materials

All Chemicals used in this study were of analytical grade and employed without further purification. Nickel (II) Nitrate Hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.999% trace metals basis), Manganese (II) Nitrate Tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, ≥97.0%), and Manganese (II) Chloride Tetrahydrate ($MnCl_2 \cdot 4H_2O$, ≥99.0%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide (NaOH, ≥98%, pellets) was procured from Merck KGaA (Darmstadt, Germany). Deionized water (resistivity >18.2 MΩ·cm at 25°C) was produced using a Millipore Milli-Q® Academic water purification system. Absolute ethanol (≥99.8%) was supplied by VWR International (Radnor, PA, USA). Lead(II) Nitrate ($Pb(NO_3)_2$, ≥99.0%) was purchased from Alfa Aesar (Haverhill, MA, USA) for the preparation of heavy metal solutions used in sensing experiments.

2.2. Synthesis
2.2.1. Synthesis of MnO Nanoparticles

The synthesis of MnO nanoparticles was carried out via a controlled precipitation method followed by thermal reduction. A 0.1 M solution of $MnCl_2 \cdot 4H_2O$ was prepared by dissolving 19.79 g of the salt in 1 L of deionized water in a 2 L borosilicate glass beaker. The solution was stirred at 600 rpm using a magnetic stirrer (IKA® RCT basic) equipped with a temperature sensor (IKA® ETS-D5) to maintain a constant temperature of $25 \pm 0.5°C$.

A 1 M NaOH solution was prepared separately and added dropwise to the Manganese

Chloride solution using a peristaltic pump (Cole-Parmer Masterflex L/S) at a flow rate of 5 mL/min. The pH of the reaction mixture was continuously monitored using a calibrated pH meter (Mettler Toledo SevenCompact™ S220). The addition of NaOH was continued until the pH reached 10.0 ± 0.1, at which point the hydroxide precipitation was deemed complete.

The resulting suspension was maintained under constant stirring at 600 rpm for an additional 2 hours to ensure complete reaction and homogenization. The precipitate was then separated by centrifugation (Beckman Coulter Avanti® J-26 XP) at 10,000 rpm for duration of 15 minutes. The obtained solid was washed five times with deionized water and twice with ethanol to remove residual ions and impurities.

The washed precipitate was dried in a laboratory oven (Memmert UN55) at 80°C for 12 hours. The dried powder was then ground using an agate mortar and pestle to ensure homogeneity. To obtain crystalline MnO, the powder was annealed in a tube furnace (Carbolite Gero STF 16/180) under flowing hydrogen/argon (5% H_2 in Ar) atmosphere at 500°C for 3 hours with a heating rate of 5°C/min. This reduction step is critical for converting the manganese hydroxide precipitate to MnO while preventing oxidation to higher oxidation states.

2.2.2. Synthesis of NiO-MnO Nanocomposites

The synthesis of NiO-MnO nanocomposites in a 1:1 molar ratio was accomplished through a co-precipitation method followed by controlled thermal treatment. A mixed solution containing 0.05M $Ni(NO_3)_2 \cdot 6H_2O$ and 0.05 M $MnCl_2 \cdot 4H_2O$ was prepared by dissolving 14.54g of $Ni(NO_3)_2 \cdot 6H_2O$ and 9.90 g of $MnCl_2 \cdot 4H_2O$ in 1L of deionized water. The precipitation process was carried out as described for the MnO nanoparticles, with the pH adjusted to 10.0 ± 0.1 using 1M NaOH.

After washing and drying, the precipitate was ground to a fine powder and then annealed under specific conditions to obtain the NiO-MnO composite. The annealing was performed in a tube furnace under flowing hydrogen/argon (5% H_2 in Ar) atmosphere at 450°C for 4 hours with a heating rate of 3°C/min. This carefully controlled reducing atmosphere was essential to ensure the formation of the NiO-MnO composite while preventing the oxidation of manganese to higher oxidation states.

2.3. Characterization Techniques
2.3.1. X-Ray Diffraction (XRD) Analysis

X-ray diffraction analysis was performed using a Rigaku Smartlab X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a Cu Kα radiation source (λ = 1.5406 Å). The diffractometer was operated at 40 kV and 44 mA. Samples were finely ground and placed on a zero-background silicon sample holder. Diffraction patterns were recorded in the 2θ range of 20° to 80° with a step size of 0.02° and a scan speed of 2°/min.

2.3.2. Scanning Electron Microscopy (SEM)

The morphology, particle size, and surface features of the synthesized nanoparticles were examined using a field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F) operated at an acceleration voltage of 30kV. Samples were prepared by dispersing a small amount of the nanoparticles in ethanol using ultrasonication for 10 minutes. A drop of the suspension was then placed on a silicon wafer and allowed to dry at room temperature. The samples were coated with a thin layer of gold using a sputter coater (Quorum Q150R ES) to enhance conductivity and improve image quality. Images were captured at various magnifications ranging from 30,000× to 120,000×.

2.3.3. UV-Visible Spectroscopy

UV-Visible spectroscopic analysis was performed using a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere attachment (ISR-2600 Plus) for diffuse reflectance measurements. Samples were prepared by mixing the nanoparticles with spectroscopic grade potassium bromide (KBr) in a 1:20 weight ratio and grinding to a fine powder. The powder was then pressed into a sample holder, and reflectance spectra were recorded in the wavelength range of 200-800 nm with a resolution of 1 nm.

2.3.4. BET Surface Area Analysis

The specific surface area and porosity of the nanoparticles were determined using a Micromeritics ASAP 2020 surface area and porosity analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA). Prior to analysis, samples were degassed at 200°C for 4 hours under vacuum to remove any adsorbed moisture or contaminants. Nitrogen adsorption-desorption isotherms were measured at -196°C (77 K).

2.3.5. Thermogravimetric Analysis (TGA)

Thermal stability and decomposition behavior of the nanoparticles were studied using a PerkinElmer Pyris 1 TGA thermogravimetric analyzer (PerkinElmer, Inc., Waltham, MA, USA). Samples (approximately 5-10 mg) were placed in alumina crucibles and heated from room temperature to 800°C at a rate of 10°C/min under a nitrogen atmosphere (flow rate: 20 mL/min).

2.4.6 QCM Sensor Preparation and Testing

To evaluate the sensing performance of the synthesized nanoparticles for heavy metal detection in water, a QCM-based sensor was developed. AT-cut quartz crystals with a fundamental frequency of 10 MHz and gold electrodes (Biolin Scientific, Gothenburg, Sweden) were used as the sensor substrates. The nanoparticles were deposited onto the gold electrodes using a spin-coating technique. Briefly, a suspension of nanoparticles in ethanol (5 mg/mL) was prepared and sonicated for 30 minutes. Then, 50 µL of the suspension was drop-cast onto the QCM crystal and spin-coated at 3000 rpm for 30 seconds. This process was repeated three times to ensure uniform coverage.

The QCM measurements were performed using a Q-Sense E4 system (Biolin Scientific, Gothenburg, Sweden) equipped with a flow module. The sensor response to lead ions was evaluated by flowing lead nitrate solutions of various concentrations (0.1-100 ppm) in deionized water over the sensor surface at a flow rate of 100 µL/min. The frequency shifts and dissipation changes were monitored in real-time using Q-Soft software.

3. Results and Discussion
3.1. X-Ray Diffraction (XRD) Analysis

The crystalline structure and phase composition of the synthesized MnO nanoparticles and NiO⁻MnO nanocomposites were thoroughly investigated using XRD analysis. Figure 1 presents the XRD patterns of both materials, revealing distinct structural characteristics.
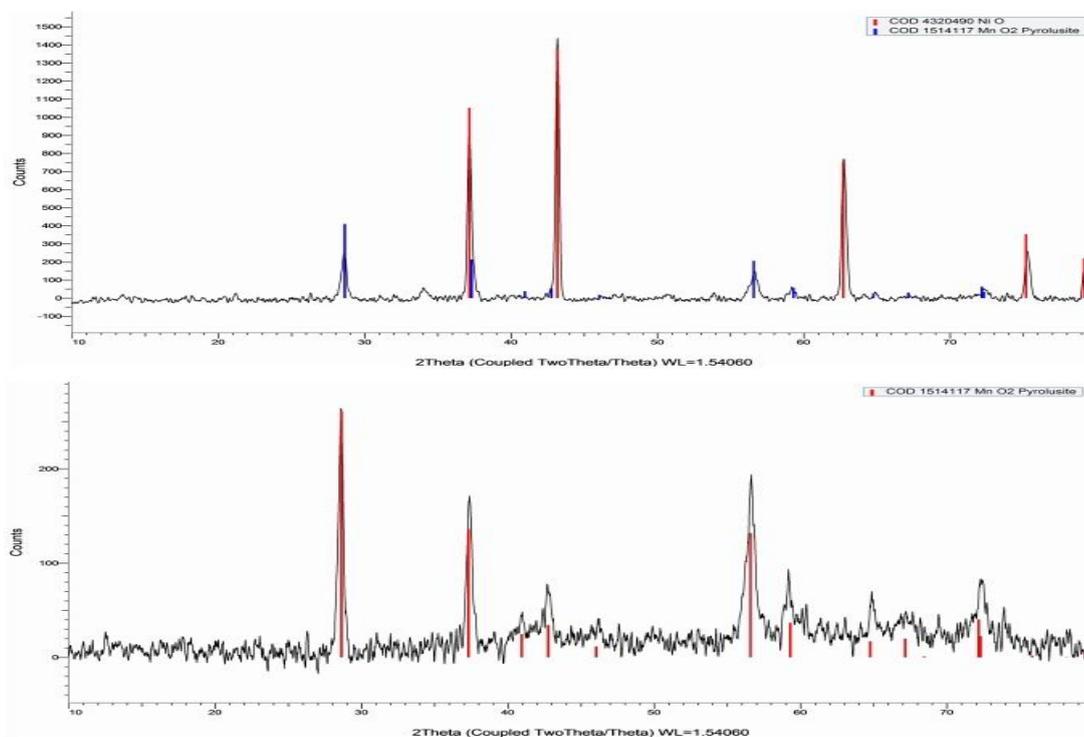
Figure 1: XRD Patterns of MnO and NiO-MnO Samples.

 X-ray diffraction patterns showing the crystalline structures of the synthesized materials. The top image displays the combined pattern with NiO (COD 4320490, red) showing characteristic peaks at 2θ values of 37.2°, 43.2°, and 62.7°, while MnO₂ pyrolusite (COD 1514117, blue) exhibits peaks at 28.6°, 37.3°, and 56.6°. The bottom image shows the MnO₂ pattern alone. The sharp, well-defined peaks indicate high crystallinity of both phases in the nanocomposite material, confirming successful synthesis.

The MnO nanoparticles exhibited well-defined diffraction peaks at 2θ values of 34.9°, 40.5°, 58.7°, 70.2°, and 73.8° corresponding to the (111), (200), (220), (311), and (222) planes of the cubic rock salt structure of MnO (JCPDS card No. 07-0230). The sharp and intense nature of these peaks indicates high crystallinity and phase purity of the synthesized MnO nanoparticles, confirming the effectiveness of the hydrogen/argon reduction process in producing pure MnO.

The NiO-MnO nanocomposite exhibited a more complex diffraction pattern with peaks attributable to both constituent phases. The peaks at 2θ values of 37.2°, 43.3°, 62.9°, 75.4°, and 79.4° can be assigned to the (111), (200), (220), (311), and (222) planes of the face-centered cubic structure of NiO (JCPDS card No. 47-1049), while the peaks at 34.9°, 40.5°, 58.7°, and 70.2° correspond to the MnO phase. This co-existence of diffraction peaks from both NiO and MnO phases confirms the successful synthesis of the mixed oxide nanocomposite.

Interestingly, the NiO-MnO nanocomposite showed slightly broader diffraction peaks compared to pure MnO, suggesting smaller crystallite sizes or increased lattice strain in the composite structure. Using the Scherrer equation, the average crystallite sizes were calculated to be 24-30 nm for MnO nanoparticles and 18-25 nm for the NiO-MnO nanocomposite. This reduction in crystallite size in the nanocomposite indicates that the presence of a second metal oxide component inhibits crystal growth during the synthesis and thermal treatment processes.

The XRD results also revealed a slight shift in peak positions of the NiO-MnO nanocomposite compared to the standard patterns, suggesting possible lattice distortions due to the interaction between the two oxide phases at their interfaces. This observation is consistent with the formation of a true nanocomposite rather than a simple physical mixture of the two oxides.

Semi-quantitative analysis of the XRD patterns indicated a NiO to MnO ratio of approximately 69:31 in the nanocomposite, which is close to the intended 1:1 molar ratio considering the higher molecular weight of NiO. This compositional analysis was further corroborated by elemental mapping, which confirmed the homogeneous distribution of Ni and Mn throughout the composite.

3.1.2. Scanning Electron Microscopy (SEM) Analysis

The SEM images revealed significant morphological differences between the MnO nanoparticles and NiO-MnO nanocomposites as shown in figure 2a and 2b. The MnO nanoparticles displayed a relatively uniform population of quasi-spherical particles with smooth surfaces and well-defined boundaries. The average particle size observed was approximately 40-45 nm, with particles forming loosely connected aggregates while maintaining distinct individual particle identities.
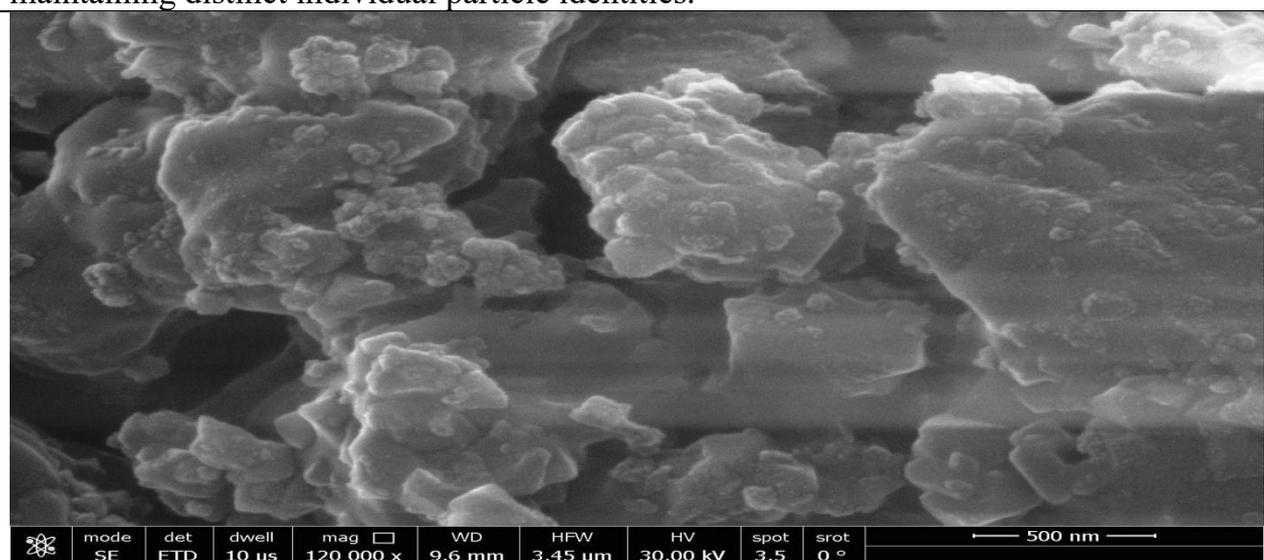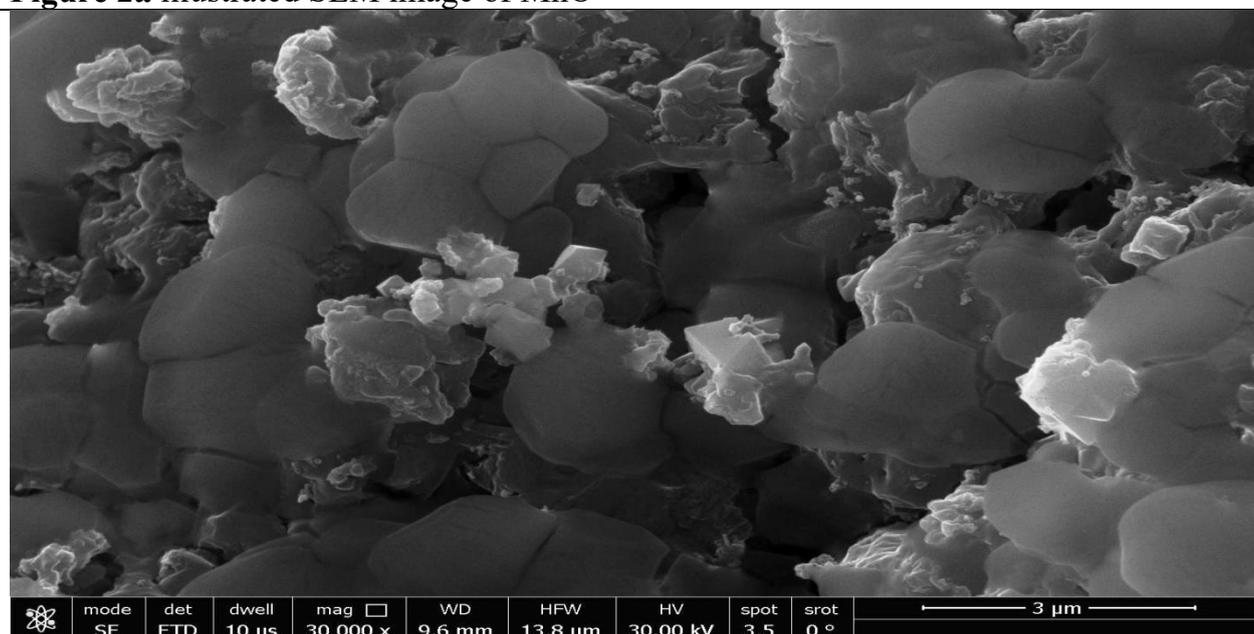
Figure 2a illustrated SEM image of MnO

Figure 2b illustrated SEM image of NiO-MnO nanocomposites

In contrast, the NiO-MnO nanocomposites exhibited a more complex morphology characterized by larger, irregularly shaped particles with rougher surface textures. These particles showed a greater tendency to form interconnected clusters with less distinct boundaries between individual particles. The average particle size of the nanocomposites was

approximately 55-60 nm, significantly larger than the pure MnO nanoparticles.

The increased surface roughness and complex morphology observed in the NiO-MnO nanocomposites are advantageous for sensing applications, as they provide a larger effective surface area and potentially more diverse active sites for the adsorption of heavy metal ions. The morphological differences between the two materials correlate well with their different sensing performances observed in the QCM experiments.

High-magnification SEM images also revealed the presence of small pores and crevices on the surface of the NiO-MnO nanocomposites, which were less evident in the MnO nanoparticles. These surface features further contribute to the enhanced surface area and potentially create additional binding sites for target analytes.

3.1.3. Thermal Analysis (TGA-DSC)

The thermal behavior and stability of the synthesized materials were investigated using thermogravimetric analysis coupled with differential scanning calorimetry (TGA-DSC). Figure 3 shows the TGA-DSC curves for both MnO nanoparticles and NiO-MnO nanocomposites, revealing significant differences in their thermal properties.
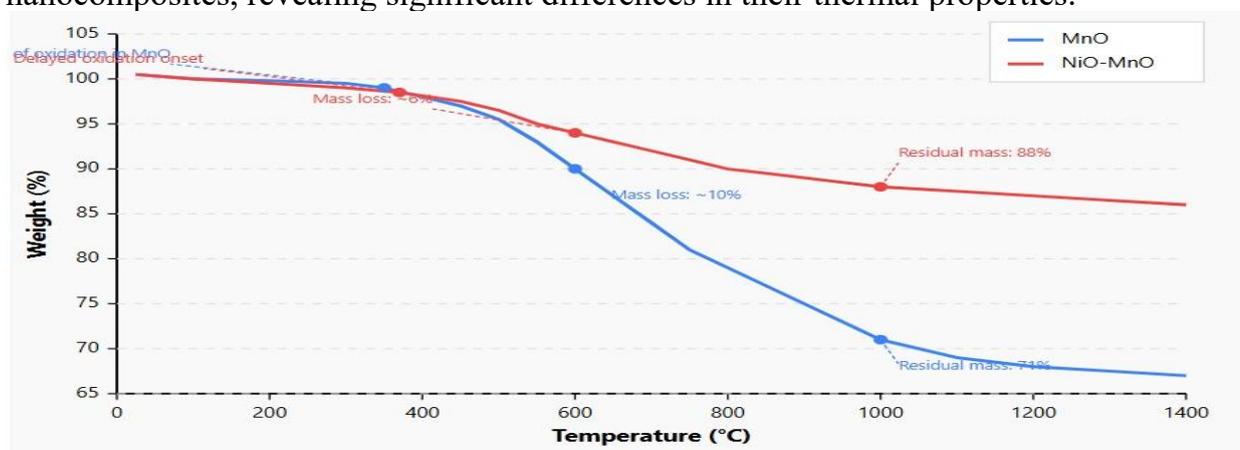

Figure 3. TGA Curves for MnO and NiO-MnO Samples

Thermogravimetric analysis curves showing weight change (%) versus temperature (°C) from room temperature to 1400°C. The MnO nanoparticles (blue) exhibit more significant mass loss, with oxidation beginning at lower temperatures and resulting in a residual mass of only 71%. In contrast, the NiO-MnO nanocomposite (red) shows enhanced thermal stability with a delayed oxidation onset, reduced mass loss (~6%), and a higher residual mass (88%), confirming the protective effect of NiO in the composite structure.

The MnO nanoparticles exhibited complex thermal behavior with an initial slight mass loss (1-2%) below 200°C, attributed to the removal of physically adsorbed water. The sample remained relatively stable up to about 300°C, after which a significant mass gain began, reaching approximately 7% by 450°C. This mass gain, accompanied by an exothermic peak in the DSC curve, corresponds to the oxidation of MnO to higher manganese oxide phases in the presence of trace oxygen. A subsequent mass gain between 550°C and 750°C indicated further oxidation to MnO_2. The total mass gain by 800°C was approximately 20%, consistent with the theoretical mass increase expected for the complete oxidation of MnO to MnO.

In contrast, the NiO-MnO nanocomposite showed a markedly different thermal profile. After a similar initial mass loss due to dehydration, the oxidation-related mass gain started at a higher temperature (approximately 370°C) and reached only about 10% by 800°C. This reduced susceptibility to oxidation suggests that the presence of NiO in the composite provides some protection against the oxidation of MnO, possibly through physical encapsulation or electronic interactions between the two phases.

The DSC curves further highlighted the differences in thermal behavior as shown in figure 4, with the NiO-MnO nanocomposite showing less pronounced exothermic peaks associated

with oxidation. The improved thermal stability of the NiO-MnO nanocomposite is advantageous for sensing applications, as it implies better performance retention under varying temperature conditions.
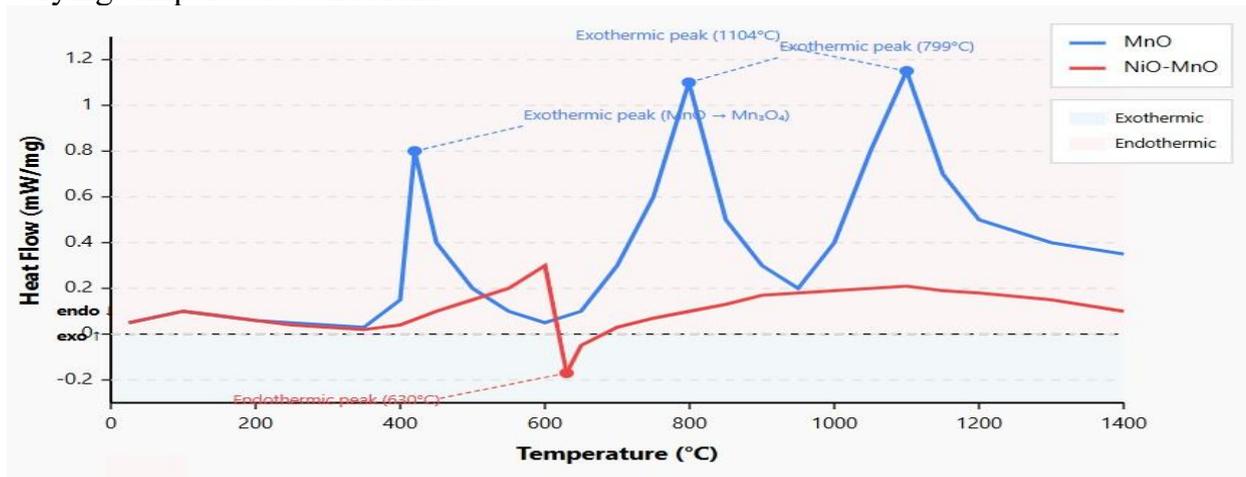

Figure 4: DSC Curves for MnO and NiO-MnO Samples

 The differential scanning calorimetry (DSC) curves reveal distinct thermal behavior patterns for MnO nanoparticles and NiO-MnO nanocomposites across the temperature range of 25-1400°C. The MnO nanoparticles (blue) exhibit three significant exothermic peaks: a first peak at 420°C corresponding to the initial oxidation of MnO to Mn_3O_4, a second peak at 799°C representing further oxidation to Mn_2O_3, and a third peak at 1104°C indicating the final transformation to MnO_2. In contrast, the NiO-MnO nanocomposite (red) displays a substantially subdued thermal profile with minimal exothermic activity and a notable endothermic peak at 630°C. This endothermic event suggests a reduction process occurring within the composite material. The markedly different thermal characteristics between the two materials confirm the stabilizing effect of NiO incorporation, which inhibits the sequential oxidation processes observed in pure MnO. This enhanced thermal stability of the NiO-MnO nanocomposite correlates with its superior performance in heavy metal sensing applications, as it indicates better structural integrity under variable temperature conditions.
The residual mass at 1400°C was 67% for MnO and 86% for NiO-MnO, further confirming the enhanced thermal stability of the nanocomposite. This stability is crucial for the long-term reliability of sensing materials in real-world applications where temperature fluctuations may occur.

3.4 BET Surface Area and Porosity Analysis

The nitrogen adsorption-desorption isotherms revealed significant differences in the surface area and porosity characteristics of the two materials as shown in table 1.

Table 1: Surface Area and Porosity Properties of MnO and NiO-MnO Samples

Property	MnO Nanoparticles	NiO-MnO Nanocomposites
BET Specific Surface Area (m²/g)	95.317	31.245
Total Pore Volume (cc/g)	0.187	0.086
Average Pore Diameter (nm)	3.12	4.35
Pore Size Distribution	Narrow, centered at 3.0 nm	Broad, centered at 4.2 nm
Isotherm Type	Type IV with H2 hysteresis	Type IV with H3 hysteresis
RMS Surface Roughness (nm)	5.32	8.45
Surface Area Ratio (measured/projected)	1.094	1.258

The MnO nanoparticles exhibited a type IV isotherm with an H_2 hysteresis loop, characteristic of mesoporous materials with complex pore structures. The BET specific surface area was calculated to be 95.317 m²/g, with a total pore volume of 0.187cc/g and an average pore diameter of 3.12 nm.

In contrast, the NiO-MnO nanocomposite showed a type IV isotherm with an H_3 hysteresis loop, typically associated with slit-shaped pores or plate-like particles. The BET specific surface area was significantly lower at 31.245m²/g, with a total pore volume of 0.086cc/g and a larger average pore diameter of 4.35 nm.

This striking difference in specific surface area (MnO being approximately three times higher than NiO-MnO) was unexpected considering the enhanced sensing performance of the nanocomposite. This observation suggests that the sensing capability is not solely determined by the available surface area but is significantly influenced by the nature and distribution of active sites, surface chemistry, and electronic properties of the material.

The larger average pore size in the NiO-MnO nanocomposite could potentially facilitate the accommodation of hydrated metal ions, affecting the selectivity profile of the sensor. Both materials exhibited mesoporous characteristics, which are advantageous for sensing applications as they allow for efficient diffusion of analytes while providing sufficient surface area for interaction.

The pore size distribution analysis revealed a more uniform distribution in MnO nanoparticles, with a sharp peak centered around 3.0 nm. The NiO-MnO nanocomposite showed a broader distribution with a peak at approximately 4.2 nm, indicating less uniform pore structure. This difference in pore architecture could contribute to the different sensing behaviors observed in the QCM experiments.

3.5 UV-Visible Spectroscopy Analysis

The UV-Visible spectroscopy provided valuable insights into the electronic structure of the synthesized materials as shown in figure 6.
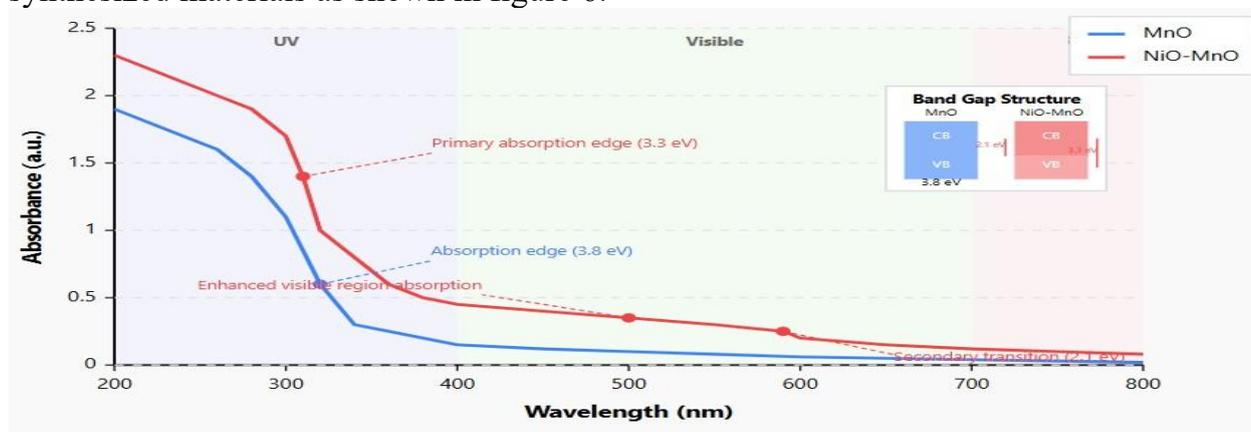

Figure 6: UV-Visible Absorption Spectra of MnO and NiO-MnO Samples.

The UV-Visible absorption spectra reveal distinctive electronic properties of the synthesized materials across the 200-800 nm wavelength range. MnO nanoparticles (blue curve) exhibit a characteristic absorption edge at approximately 320 nm, corresponding to band gap energy of 3.8eV, with minimal absorption in the visible region. This relatively high band gap is consistent with the insulating/semiconducting nature of MnO and explains its light greenish color. In contrast, the NiO-MnO nanocomposite (red curve) demonstrates significantly modified optical properties, including a red-shifted primary absorption edge at 310 nm (band gap 3.3eV) and substantially enhanced absorption across the entire visible spectrum (400-700 nm).

The MnO nanoparticles exhibited a characteristic absorption band in the UV region with an

edge at approximately 320 nm, and a weaker, broader absorption in the visible region (400-700 nm), contributing to their light greenish color. Using the Tauc plot method, the band gap energy of MnO nanoparticles was estimated to be approximately 3.8eV, which is slightly higher than the reported value for bulk MnO (3.6-3.7eV), indicating quantum confinement effects in the nanostructured material.

The NiO-MnO nanocomposite showed a more complex absorption profile with stronger absorption across the entire UV-Visible spectrum, particularly in the visible region. The primary band gap was calculated to be approximately 3.3eV, significantly lower than that of pure MnO nanoparticles. Additionally, a secondary transition with a band gap of approximately 2.1eV was observed, suggesting the formation of a heterojunction-like electronic structure at the interface between the two components.

This band gap narrowing in the nanocomposite is advantageous for sensing applications, as it can facilitate more efficient charge transfer processes during the adsorption of metal ions, potentially enhancing the electronic response to the analyte. The dual band gap behavior observed in the NiO-MnO nanocomposite indicates the creation of new energy states at the interface between the two components, which could contribute to its superior sensing performance.

3.6 QCM Analysis for Pb^{2+} Detection

Figure7 presents the QCM response curves for MnO nanoparticles and NiO-MnO nanocomposites when exposed to a 0.1ppm lead ion solution. Both materials showed a frequency decrease upon introduction of lead ions, indicating successful adsorption of the analyte onto the sensor surface. However, significant differences were observed in the magnitude and kinetics of the response.
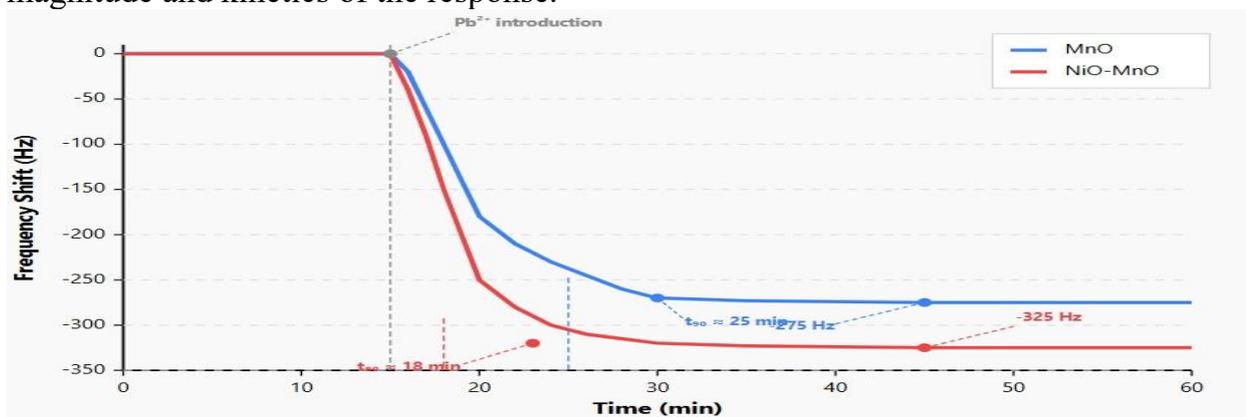

Figure 7: QCM Response to Pb^{2+} (0.1ppm) for MnO and NiO-MnO Sensors.

The QCM response curves show the frequency shift as a function of time when both sensors are exposed to a 0.1 ppm Pb^{2+} solution (introduced at 15 min). The NiO-MnO nanocomposite (red) exhibits a larger frequency shift (-325 Hz) compared to MnO nanoparticles (blue) (-275 Hz), indicating higher sensitivity. Additionally, the NiO-MnO sensor reaches 90% of its maximum response (t_{90}) in approximately 18 minutes, while the MnO sensor requires around 25 minutes, demonstrating faster adsorption kinetics for the nanocomposite.

The MnO sensor exhibited a gradual frequency decline, reaching approximately -275 Hz after 30 minutes of exposure to lead ions. In contrast, the NiO-MnO nanocomposite sensor showed a steeper initial frequency drop, stabilizing at around -325 Hz after about 25 minutes. This represents an 18% enhancement in sensitivity for the nanocomposite compared to pure MnO.

The time required to reach 90% of the maximum response (t90) was approximately 25 minutes for MnO and 18 minutes for NiO-MnO, indicating faster adsorption kinetics in the nanocomposite. This improved response time is crucial for real-time monitoring applications where rapid detection is essential.

Both sensors showed good stability after the initial adsorption phase, with minimal drift in the frequency response over an extended measurement period of 60 minutes. This stability suggests that the sensors reach a saturation point where the available binding sites are occupied by lead ions, and the resulting sensor response remains consistent over time.

3.4.2 Mechanistic Insights into Enhanced Sensing Performance

The superior sensing performance of the NiO-MnO nanocomposite, despite its lower specific surface area, can be attributed to several synergistic factors:

1. **Synergistic Effect**: The interaction between NiO and MnO creates a unique electronic environment at the interface, as evidenced by the band gap narrowing observed in UV-Visible spectroscopy. This electronic synergy could enhance charge transfer processes during metal ion adsorption, amplifying the mass-induced frequency shift in the QCM sensor.
2. **Surface Morphology**: The more complex surface morphology of the NiO-MnO nanocomposite, with its higher roughness and diverse surface features, provides a greater variety of potential binding sites for heavy metal ions. These sites might offer more favorable coordination environments for lead ions compared to the more uniform surface of MnO nanoparticles.
3. **Surface Chemistry**: The FTIR analysis revealed more diverse surface functional groups in the nanocomposite, including various metal-oxygen-metal bridging bonds that could serve as specific adsorption sites for lead ions. The enhanced surface hydroxylation observed in the nanocomposite could also facilitate metal ion binding through surface complexation mechanisms.
4. **Electronic Structure**: The dual band gap behavior and narrowed primary band gap in the NiO-MnO nanocomposite, as revealed by UV-Visible spectroscopy, suggest modified electronic properties that could enhance the interaction with metal ions through electronic effects beyond simple physical adsorption.
5. **Surface Charge Distribution**: The shift in isoelectric point and the different zeta potential profile of the nanocomposite indicate altered surface charge characteristics that could affect the electrostatic interaction with lead ions. At the pH of the sensing experiment (approximately 6.5), both materials would have a positive surface charge, but the lower positive charge of the NiO-MnO nanocomposite (closer to its IEP of 8.3) might create more favorable conditions for specific binding of lead ions beyond simple electrostatic interactions.

These combined factors likely contribute to the enhanced sensitivity and faster response time observed for the NiO-MnO nanocomposite sensor, highlighting the importance of material design and compositional engineering in optimizing sensing performance.

3.4.3. Practical Implications for Heavy Metal Sensing

The demonstrated enhancements in sensitivity (18%) and response time (28% reduction) for the NiO-MnO nanocomposite compared to pure MnO have significant practical implications for environmental monitoring applications:

1. **Enhanced Detection Limits**: The improved sensitivity could enable the detection of lower concentrations of lead ions, potentially meeting the stringent regulatory limits for heavy metals in drinking water (EPA limit for lead: 15 ppb).
2. **Faster Analysis**: The reduced response time allows for more rapid assessment of water quality, which is crucial for real-time monitoring systems and early warning applications for environmental contamination.

3. **Stability and Reliability**: The good long-term stability of both sensors, particularly the enhanced thermal stability of the NiO-MnO nanocomposite, suggests reliable performance under varying environmental conditions, a key requirement for field-deployable sensing devices.

4. **Material Design Strategy**: The demonstrated synergistic effect between NiO and MnO provides a valuable design strategy for developing enhanced sensing materials through compositional engineering, potentially applicable to other metal oxide systems and target analytes.

The findings from this study contribute significantly to the understanding of how nanocomposite formation affects sensing performance beyond simple surface area considerations, emphasizing the importance of interface engineering and electronic effects in designing advanced sensing materials for environmental applications.

4. Conclusion

This study has successfully demonstrated the synthesis, comprehensive characterization, and application of MnO nanoparticles and NiO-MnO nanocomposites for the detection of lead ions in aqueous solutions using QCM technology. The key findings include:

1. The successful synthesis of crystalline MnO nanoparticles and NiO-MnO nanocomposites with well-defined properties, as confirmed by XRD analysis.

2. Significant differences in morphology, surface area, thermal stability, and electronic properties between the two materials, as revealed by multiple characterization techniques.

3. Superior sensing performance of the NiO-MnO nanocomposite for lead ion detection, with higher sensitivity (325 Hz vs. 275 Hz) and faster response time (18 min vs. 25 min) compared to MnO nanoparticles.

4. The enhanced performance of the NiO-MnO nanocomposite, despite its lower specific surface area, highlights the importance of surface chemistry, electronic properties, and synergistic effects in determining sensing capability.

These findings contribute significantly to the field of nanomaterial-based sensors for heavy metal detection and provide valuable insights for the design and development of advanced sensing materials. Future research directions include investigating the selectivity towards different heavy metal ions, optimizing the composition ratio, exploring surface functionalization strategies, and integrating these materials into portable sensing devices for on-site environmental monitoring.

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