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Evaluation of Mn3O4NPs Synthesize for Enhanced Electrochemical Sensors

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Abstract: *The presence of heavy metal contamination has the potential to impact many organs, such as the brain, lungs, kidneys, liver, and other bodily systems, leading to detrimental effects on both the immunological and nervous systems of humans. There is a need for a device with an inexpensive electrode, high accuracy and sensitivity, user-friendliness, dependability, and applicability in the field. The electrochemical sensor is the most promising of all sensors. However, surface modification of the active electrode is essential to enhancing its signal, sensitivity, and detection speed. Mn3O4NPs were synthesised using the co-precipitation method in this study. The Mn3O4 nanoparticles were subjected to characterization by X-ray diffraction (XRD), Transmission Electron Microscopy, and Zeta potential analysis. The X-ray diffraction (XRD) investigation revealed that the Mn3O4 nanoparticles exhibited a tetragonal morphology, with an average crystallite size diameter of around 38nm. The notable size of Mn3O4NPs has the potential for application as a modified electrode in electrochemical sensors, specifically to detect heavy metals.*

Keywords: *Characterization, Electrochemical sensors, Heavy metals, Nanoparticles, Tri-manganese IV Tetra-oxide, Voltammetry.*

1.0 Introduction

Excessive ingestion of heavy metals has the potential to adversely affect the central nervous system, leading to anomalies in the blood and brain of mammals. Cadmium, arsenic, lead, and mercury are commonly associated with heavy metal contamination (Wang et al., 2017). Heavy metals such as manganese, iron, zinc, and copper are essential for maintaining a state of well-being, albeit in relatively modest quantities. The gradual accumulation of heavy metals throughout the food chain can

significantly harm human health (Lee et al., 2016). Determining heavy metal levels is crucial in mitigating the adverse impacts on mammals, aquatic organisms, animals, and terrestrial plants (Duodu et al., 2016). Various techniques have been employed to determine metal ion concentrations, such as atomic absorption spectroscopy (AAS) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The conventional procedures employed in detecting heavy metal ions are often regarded as reliable. Although the traditional approaches possess selectivity and high sensitivity, they have notable limitations. These include costly equipment requirements, intricate operational procedures, extended detection durations, and difficulty detecting actual samples in field conditions (Lee et al., 2016). Therefore, sensors are deemed more favourable to address these limitations.

Electrochemical sensors exhibit considerable potential for detecting heavy metals within sensor technology. Stripping voltammetry, an electrochemical technique, is highly regarded and holds great promise due to its exceptional characteristics, including cost-effectiveness in equipment, little power usage, rapid analysis time, and high sensitivity (Borrill et al., 2019). The efficacy of bulk electrodes in detecting heavy metals is limited, necessitating modifications to boost sensitivity and reduce the limit of detection (LOD). The limited active surface area of the electrode results in diminished sensitivity and selectivity of the electrochemical sensor. The utilisation of a mercury electrode in electrochemical sensors is highly advantageous owing to its remarkable ability to pre-concentrate heavy (Lee et al., 2016).

Nevertheless, due to the inherent toxicity of mercury, there is a growing demand for alternative electrode materials that are free from mercury. Bismuth emerges as a highly attractive substitute electrode for electrochemical measurements due to its comparable performance to mercury. The features of bismuth are associated with its propensity to create a "fused alloy" with heavy metals and undergo oxidation in the presence of air, rendering it non-sustainable (Bagheri et al., 2015).

Using nanomaterials as electrode modifiers has demonstrated significant advancements in enhancing selectivity, linearity, catalytic activity, sensitivity, and other essential parameters in electrochemical detection (Yan & Wang, 2017). Nanomaterials, including metal/metal oxide and carbon-based nanoparticles, have significantly advanced sensing applications due to their remarkable properties. These properties include chemical inertness, a high surface area to volume ratio, a tuneable band gap, ease of chemical modification, quantum effects, high electron communication features, biocompatibility, and ease of synthesis (Chen et al., 2016).

Tri-manganese tetra-oxide nanoparticles (Mn_3O_4NPs) possess several distinctive characteristics that set them apart from other metal oxide nanoparticles. These include their cost-effectiveness, ease of synthesis, exceptional electrochemical stability, versatility in shape, impressive theoretical capacitance, notable catalytic activity, environmentally friendly nature, and ability to deliver a high charge rapidly. The study by Zhou et al. (2018) demonstrates the efficacy of Mn_3O_4NPs as a catalyst in facilitating the redox transformation of several organic compounds, including NH_4, CO_2, and $C_6H_5NO_2$. Manganese (III) oxide nanoparticles (Mn_3O_4 NPs) have extensive applications in several

fields, such as sensor technology, catalyst development, alkaline cells, and lithium-ion batteries.

Numerous researchers have reported the utilisation of electrodes modified with nanomaterials as a promising alternative for heavy metal ion sensors. This is attributed to the remarkable properties exhibited by nanomaterials, including enhanced surface kinetics, increased electrochemical reaction efficiency through the expansion of the electroactive surface area, and improved adsorption of analytes on the electrode surface. These characteristics collectively contribute to enhancing electrode sensitivity, selectivity, and analyte adsorption, as Dang et al. (2015) highlighted. Poor adhesion between the electrode and nanomaterial reduces heavy metal detection sensitivity and increases the limit of detection (LOD) of the modified electrode. However, Nafion is needed to prevent nanoparticle-electrode interference, boost sensitivity, and lower LOD.

In their study, Hao et al. (2016) conducted a hydrothermal synthesis to produce three-dimensional arrays of manganese dioxide nanowires (MnO_2 NWAs) on nickel foam (MnO_2/NF). These arrays were then employed as an electrochemical sensor to detect copper ions (Cu^{2+}). The detection technique utilised was SWASV, and the limit of detection (LOD) achieved was 0.17μM. The synthesis of a glassy carbon disc modified with a nanocomposite of gold and manganese oxide (Au/MnO_2) was reported by Wei et al. (2018). The process of electrochemical deposition achieved the modification. The modified electrode exhibited exceptional sensitivity in detecting heavy metal ions and has been successfully employed in practical applications for sensing heavy metals in seawater (Sukhdev et al., 2020).

The utilisation of tri-manganese tetra-oxide nanoparticles (Mn_3O_4NPs) as an electrode modifier has garnered attention in the scientific community. This interest stems from the numerous advantages of Mn_3O_4NPs, including their environmentally friendly nature, exceptional stability, low toxicity, and remarkable catalytic activity. These characteristics render Mn_3O_4NPs a suitable nanomaterial for electrode modification, particularly in the context of heavy metal ion detection.

2.0 Research Methodology

2.1 Materials and Methods

All chemicals and materials were utilised in their original, unaltered state. The production of tri-manganese (IV) tetra-oxide nanoparticles (Mn_3O_4NPs) involves the utilisation of sodium hydroxide (NaOH) and manganese acetate tetrahydrate as the primary materials and chemicals. In contrast, the substances employed for the fabrication and maintenance of indium tin oxide (ITO) coated glass as the working electrode encompass ITO-coated glass, hydrogen peroxide (H_2O_2), ammonia hydroxide (NH_4OH), propanol (C_3H_8O), and distilled water.

The materials and chemicals employed in the electrode modification process consist of tri-manganese (IV) tetra-oxide nanoparticles (Mn_3O_4NPs), ethanol, and Nafion. The components used in electrochemical tests encompass many raw materials and chemicals, including a counter electrode composed of platinum, a reference electrode consisting of silver/silver chloride (Ag/AgCl), as well as potassium ferricyanide,

potassium chloride, and an acetate buffer solution. Table 2.1 presents comprehensive information regarding the materials and chemicals employed in the present research study.

Table 2.1: Details of raw materials and chemical used for the research work.

Process	Chemical/ reagent	function	CAS No	Assay (%)	Manufacture details (g/mol)	Supplier
Synthesis of Mn_3O_4NPs	Manganese (II) acetate tetrahydrate $(CH_3COO)2Mn\cdot4H_2O$)	Precursor	6156-78-1	99.99	Mw= 245.09	Sigmal Adrich
	Sodium hydroxide (NaOH)	Reducing agent	1310-73-2	97.0	M w=39.997	Merck

2.2 The Synthesis of Mn3O4NPs

The synthesis of tri-manganese (IV) tetra-oxide (Mn3O4NPs) was accomplished using a co-precipitation technique. This method possesses several notable attributes compared to alternative procedures, such as its ecologically benign nature, minimal equipment requirements, and ease of handling. In this experiment, a solution of sodium hydroxide (NaOH) with a concentration of 0.25M was employed as a precursor. In comparison, a solution of manganese acetate tetrahydrate (C4H16MnO8) with a concentration of 0.1M was utilised as a reducing agent. Sodium hydroxide was incrementally introduced into manganese acetate tetrahydrate at a stirring speed of approximately 300 revolutions per minute until the pH reached 12.

The sediments were subjected to filtration using a Whatman filter paper. The precipitates were washed using distilled water to achieve a neutral pH value of approximately 7. The obtained deposits were subjected to drying at 80°C overnight in an oven. The sediments were pulverised using a mortar and pestle. According to Singh et al. (2021), the chemical reaction during the synthesis of Mn3O4NPs is expressed in equation 2.1 and 2.2.

$$Mn(CHOO)_2.4H_2O+NaOH \rightarrow Mn(OH)_2 +4H_2O.2CH_3COONa \quad 2.1$$

$$Mn(OH)_2 \rightarrow Mn_2O_3+1/2\ O_2 \quad 2.2$$

3.0 Result and Discussion

3.1 Characterization of Mn3O4NPs' Structure and Morphology

The co-precipitation approach was employed to synthesize Mn3O4NPs in this study. The X-ray diffraction (XRD) technique was used to examine the synthesized manganese oxide nanoparticles' phase presence and crystal structure (Mn3O4NPs). The X-ray diffraction (XRD) pattern of the Mn3O4NPs in their original synthesized state is depicted in Figure 3.1. The diffraction peaks observed in the data can be attributed

to Mn3O4NPs, which possess a tetragonal structure commonly known as Haus-mannite (ICDD 89-4837). The X-ray diffraction (XRD) pattern exhibits the absence of characteristic peaks corresponding to MnO, MnO2, or Mn2O3, indicating a high level of purity, which has been corroborated by previous studies (Chang et al., 2004).

The diffraction peaks observed for Mn3O4NPs are located at specific angles, namely 18º, 28.9º, 31.0º, 32.3º, 36.1º, 37.9º, 44.4º, 50.7º, 53.8º, 56.0º, 58.5º, 59.8º, 64.6º, 78.4º, 80.2º, and 86.3. These peaks correspond to the crystallographic planes (011), (112), (020), (013), (121), (004), (220), (015), (132), (033), (231), (244), (040), (143), and (145) as indexed by the International Centre for Diffraction Data (ICDD) with reference number 89-4837. These findings suggest that the Mn3O4NPs synthesized using the co-precipitation method exhibit high crystallinity and purity. The determination of the crystallite size of the Mn3O4NPs synthesized was carried out by analyzing the prominent diffraction peaks of the (121) plane and applying the Scherrer formula.

$$d = {B\lambda}/{(\beta Cos\theta)} \qquad 3.1$$

The B constant, around 0.94, represents a specific value. The λ symbol denotes the X-ray wavelength utilized in X-ray diffraction (XRD), measured at 1.5418 Å. The θ symbol represents the Bragg angle, while β signifies the pure diffraction widening of a peak at half-height. The diameter of the nanoparticles, as determined by the Scherrer formula, is 38nm.

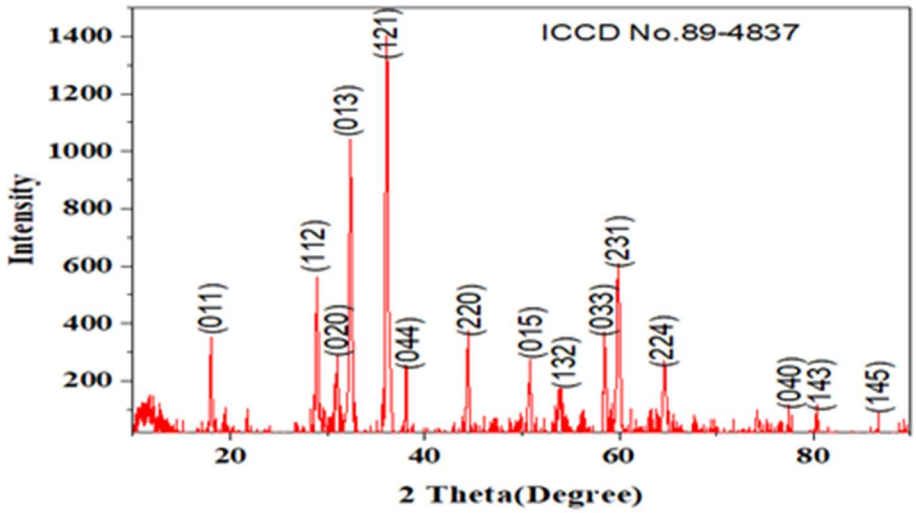

Figure 3.1 displays the manganese oxide nanoparticles' X-ray diffraction (XRD) pattern (Mn3O4NPs) in their as-synthesized state.

The morphology and size distribution of manganese(III) oxide nanoparticles (Mn3O4NPs) were analysed utilising a Transmission Electron Microscope (TEM). Figure 3.2(a) depicts the image displaying the square shape-morphology of Mn3O4NPs. The statistical study of the diameter distribution of Mn3O4NPs is shown in Figure 3.2(b). The data provided indicates that the average diameter is roughly 35 nanometers. The synthesis parameter was not adjusted to modify the particle size in this study. According

to Rani et al. (2018), the average diameter of Mn3O4NPs is influenced by the growth temperature, with a reduced average diameter observed at lower growth temperatures.

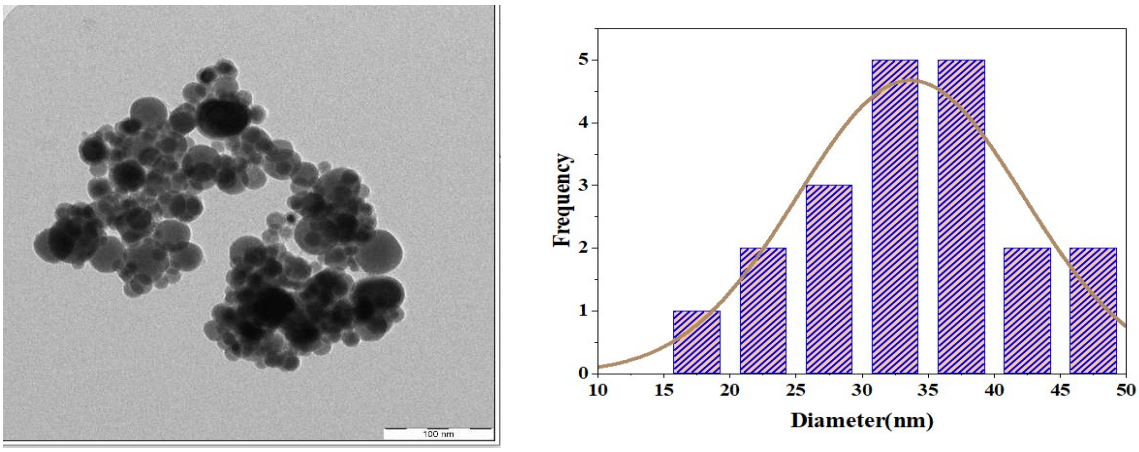

Figure 3.2: (a) TEM image of Mn3O4NPs; (b) histogram for the diameter distribution of Mn3O4NPs

3.2 Zeta Potential and Electrical conductivity of Mn3O4NPs

The zeta potential (ζ) is a parameter used to characterise the stability of colloidal dispersions. Before changing the electrodes, it is imperative to conduct this investigation to ensure the achievement of uniformly distributed nanoparticles on the electrodes. Theoretically, it is expected that aqueous systems with a zeta potential over 30 mV will exhibit increased stability in their dispersions.

The analysis of zeta potential is primarily influenced by the chemical composition of the surface sample, as well as the presence and characteristics of the dispersant. The zeta potential of Mn3O4 nanoparticles in ethanol was measured to be +33.2 mV. According to Kashyap, Mishra, and Behera (2014), particles with zeta potentials falling below -30 mV or above +30 mV are known to demonstrate a notable stability level primarily due to interparticle electrostatic repulsion. The findings of this study indicate that the Mn3O4 nanoparticles remained stable in their colloidal state.

4.0 Conclusions

The co-precipitation technique effectively achieved the synthesis of Mn3O4NPs. This method possesses several notable attributes compared to alternative procedures, such as its ecologically benign nature, minimal equipment requirements, and ease of handling. The synthesis of Mn3O4NPs yielded significant findings, including a crystallite size of 38 nm as determined by XRD examination, an average diameter size of 35 nm observed using TEM, and a Zeta Potential of +33.2 mV. In addition, the notable size of Mn3O4NPs has the potential for application as a modified electrode in electrochemical sensors, specifically to detect heavy metals.

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