



From nanodots to nanowires: simple ion-controlled morphology engineering of manganese oxide nanostructures

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Abstract

This study presents a simple and cost-effective approach for morphology control of manganese oxide (MnOx) nanomaterials through manipulation of reaction stoichiometry and post-synthesis processing. By systematically varying the molar concentration of hydrochloric acid (HCl) and applying controlled rinsing steps, a transition from nanoparticle-dominated (0D) to nanorod-rich (1D) morphologies was achieved without the use of templates or advanced fabrication techniques. Six samples synthesized under different conditions were characterized using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopy (EDX). The results suggest that morphology evolution is governed by a growth regime defined by the balance between Mn^{2+} generation, Mn^{2+} stabilization, and the resulting MnO_2 supersaturation. Within the studied range, increased acidity enhances Mn^{2+} generation and promotes MnO_2 formation, leading to higher effective supersaturation and the onset of anisotropic growth. In this framework, residual potassium (K^+)-containing species are interpreted as secondary, growth-modifying factors that may influence the extent of anisotropy, rather than as primary determinants of phase formation or morphology. EDX analysis indicates a qualitative reduction in residual K content following rinsing, although these measurements remain semi-quantitative. The relationship between K content and morphology is therefore interpreted cautiously, as the effective K^+ -to- MnOx ratio is not directly measured and cannot be decoupled from concurrent changes in ionic strength and chloride concentration. Overall, these findings highlight the coupled roles of reaction stoichiometry and ion-mediated growth in shaping MnOx nanostructures, and demonstrate a simple, scalable strategy for morphology engineering in manganese oxide systems.

Keywords

Manganese oxide nanostructures, Nanorod growth, Reaction stoichiometry, Supersaturation-controlled synthesis, Ion-assisted growth, Potassium ion effects, Anisotropic crystal growth, Template-free synthesis, Morphology engineering, Energy storage materials

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1. Introduction

Nanotechnology is the manipulation and control of matter at the nanoscale, typically between 1 and 100 nanometers. At this scale, materials exhibit unique physical, chemical, electrochemical, and biological properties that differ profoundly from their bulk counterparts. This has opened new frontiers in science and engineering, enabling advancements in diverse fields such as medicine, electronics, environmental science, and energy (1-3).

The importance of nanotechnology lies in its ability to enhance material performance and create innovative solutions to global challenges. Applications range from targeted drug delivery systems to ultra-sensitive sensors, water purification systems, and renewable energy technologies. Among these, its role in energy generation and storage is especially vital as the world shifts toward sustainable energy sources (4,5).

Nanomaterials are substances with structural components smaller than 100 nanometers in at least one dimension. They include nanoparticles (zero dimension, 0D), nanotubes/nanowires (1D), and thin films (2D). Due to their high surface area-to-volume ratio, quantum effects, and tunable properties, nanomaterials are capable of revolutionizing conventional technologies (6,7). Their importance spans several domains: in electronics, they enable the miniaturization of components; in medicine, they support personalized therapies; and in energy, they enhance the performance of batteries, fuel cells, and solar cells. The functionality of

nanomaterials is often defined by their morphology, composition, and crystalline structure, which can be precisely engineered for specific applications (8,9).

The energy sector has greatly benefited from the integration of nanomaterials in both generation and storage technologies. In energy generation, nanomaterials improve the efficiency of photovoltaic cells by enhancing light absorption and charge separation. For example, quantum dots and perovskite nanostructures have enabled high-efficiency solar cells. In energy storage, nanomaterials contribute to higher capacity, faster charging, and longer life cycles of batteries and supercapacitors. They facilitate better ion transport, increase electrode surface area, and reduce degradation. Lithium-ion batteries, fuel cells, and hydrogen storage systems are some areas where nanomaterials are making a transformative impact (10,11).

Among various nanomaterials, transition metal oxides (TMOs) such as titanium dioxide (TiO_2), nickel oxide (NiO), cobalt oxide (Co_3O_4), and manganese dioxide (MnO_2) have gained noticeable attention. Their variable oxidation states, electrochemical activity, and stability make them ideal candidates for applications in supercapacitors, lithium-ion batteries, and catalytic converters. These materials exhibit pseudocapacitance behavior, offering high power and energy densities. Their morphology, whether nanorods, nanoflakes, or mesoporous structures, can be tailored to optimize performance. The synergistic use of different TMOs in composites has also been

explored to overcome individual limitations and enhance overall efficiency (12-14).

Manganese oxide stands out among TMOs due to its low cost, abundance, environmental friendliness, and superior electrochemical performance. This material comes in various oxidation states and structures (MnO , MnO_2 , Mn_2O_3 , Mn_3O_4), which contribute to its versatility. It also exists in various polymorphic forms (α -, β -, γ -, and δ - MnO_x), each with distinct tunnel or layered structures that influence its application potential. Manganese Oxide nanomaterials are widely used in supercapacitors and battery electrodes due to their high theoretical capacitance, fast redox reactions, and stability. Their versatility also extends to catalysis, water splitting, and biosensors. Recent research focuses on improving their conductivity through doping or forming Manganese Oxide-based hybrids with carbon materials or other metal oxides (15,16).

1.1 Related work

Manganese oxide is a naturally abundant compound found in soils and sediments and has emerged as a highly versatile material in energy-related fields. Its ability to adsorb metal ions and its rich electrochemical properties make it valuable for various applications, especially in energy storage and conversion technologies. Also, by controlling the morphology of manganese oxide, its various properties can be tuned for energy-related applications. And this can be done in several ways; one of which is by simply adjusting the experimental conditions. This work on the morphological engineering of manganese oxide

integrates several of these research areas. Each area is reviewed, the existing research gaps are identified, and the key research problem is defined.

1.1.1 *Morphology engineering of manganese oxide nanomaterials*

Morphology engineering of nanomaterials refers to the deliberate control and design of their shape, size, structure, and surface characteristics at the nanoscale. This control proves essential because morphology profoundly impacts the physical, chemical, optical, electronic, and catalytic properties of nanomaterials. Mastery over morphology allows for the development of materials tailored to specific applications, placing it at the forefront of progress in nanoscience and nanotechnology (17,18).

Manganese oxides, widely studied for their structural versatility, require careful morphological control at the nanoscale. This directly affects properties such as surface area, active sites, electrical conductivity, and overall performance. For instance, manganese oxide nanoparticles (0D) exhibit strong catalytic and biomedical utility, while nanorods or nanowires (1D) excel in energy-related and sensing applications. In contrast, nanosheets or nanoplatelets (2D) find frequent use in catalysis and energy storage.

Several synthesis techniques, such as hydrothermal methods, sol-gel processes, templating, and electrodeposition, have been employed to achieve morphology control in manganese oxide nanomaterials. However,

these techniques often suffer from high cost, procedural complexity, low yield, and limited scalability. Furthermore, some resulting nanostructures degrade over time or under cycling conditions, and maintaining uniform, reproducible morphology across large batches remains a challenge (19-22).

More recently, several research groups have utilized alkali ions as growth initiators to regulate the morphology of manganese oxide nanomaterials. Yang and co-authors proposed that K^+ ions play a critical role in phase-controlled synthesis under hydrothermal conditions (23). They found that K^+ ions serve as templates for forming one-dimensional nanostructures, with the K^+ ion concentration distinctly affecting the crystallinity of MnO_2 nanowires and nanorods. Similarly, Dang, Barai, Roy, and others demonstrated morphology conversion, from nanoparticles to nanorods, by adjusting the K^+ concentration through controlled rinsing steps (24-26). Not only K^+ but also Li^+ and Na^+ ions have been reported to initiate nanorod formation in manganese oxides (27-29). This method offers a cost-effective and straightforward approach, requiring only simple adjustments to the synthesis conditions for morphological control.

1.1.2 Energy applications of manganese oxide nanomaterials

Owing to its tunable redox chemistry and structural versatility, manganese oxide (MnO_x) has been widely investigated as a functional transition-metal oxide in materials research. These characteristics have motivated extensive exploration of MnO_x across a range of energy-

related and catalytic applications, where material performance is often closely linked to composition, oxidation state, and structural organization at the nanoscale. Consequently, understanding how synthesis conditions influence MnO_x structure provides an important foundation for evaluating its application-oriented behavior.

In battery systems, MnO_x serves as an intercalation-active electrode material, particularly in lithium-ion and zinc-air batteries. Its multiple accessible oxidation states (Mn^{2+} , Mn^{3+} , Mn^{4+} , and Mn^{6+}) enable multi-electron redox processes, and hybrid MnO_x -based materials, including $MnO_2@CoMn_2O_4$ and $\alpha-MnO_2/\beta-MnO_2$ networks, have been reported to show enhanced electrochemical stability and specific capacitance compared to single-phase materials (30-32). MnO_x has also been explored for supercapacitor electrodes because of its low cost, environmental compatibility, and high theoretical capacitance, although limitations in conductivity and cycling stability often require morphology engineering or composite design strategies to improve performance (33,34).

Beyond electrochemical storage, MnO_x nanostructures such as nanorods and hollow nanotubes have been investigated for hydrogen-related applications, including hydrogen storage and electrocatalytic water splitting, due to their high surface-to-volume ratios and structural tunability (35,36). Numerous studies have reported scalable synthesis routes for MnO_x nanomaterials, including wet-chemical and acidic reduction

methods that yield diverse morphologies for environmental, catalytic, and energy-related investigations (24-26, 37-41).

More recently, environmentally benign and scalable synthesis approaches using plant extracts, microbes, biomass, and natural polymers have also been explored. Overall, the prior work highlights the importance of structure–property relationships in MnO_x nanomaterials, motivating continued investigation of morphology-controlled synthesis strategies.

1.2 Research gap and problem definition

Although previous studies have reported the morphological engineering of manganese oxides by controlling the K^+ ion concentration in the precursor solution, several gaps remain. Most of these works relied on regulating the rinsing steps during sample collection from the residual solution to adjust the ion concentration in the final product. While this approach is simple, achieving systematic modulation of the K^+ ion concentration in the final product through rinsing is inherently arbitrary, making exact regulation difficult. This work addresses this gap. Here two similarly simple strategies were employed for the controlled variation of K^+ ion concentration and thereby control the morphology of manganese oxide nanomaterials, from nanoparticle structures to nanorod structures. First, the acidic conditions of the precursor solution was modified for a possible adjustment of the $\text{K}^+ : \text{MnO}_2$ ratio during the reaction. Second, the rinsing process was tailored to further regulate the K^+ content within the synthesized samples. However, the

effective K^+ –to– MnO_x ratio is used here as a qualitative descriptor and is not presented as a directly measured quantity.

Therefore, this study represents a controlled experimental demonstration of how reaction stoichiometry defines the growth regime, within which alkali ions may modulate morphology. It demonstrates how simple, low-cost synthesis modifications can effectively engineer the morphology of manganese oxide nanomaterials into low-dimensional nanostructures (from 0D nanodots to 1D nanorods) without using complex equipment, templates, or expensive fabrication methods. Also, a qualitative alkali-ion-assisted growth model is proposed for this morphology evolution. However alternative explanations based on changes in ionic strength or chloride-mediated growth cannot be fully excluded.

1.3 Design

The objective of this study was to investigate how synthesis conditions influence the morphology of manganese oxide nanomaterials. Specifically, simple parameters such as precursor concentration, reaction conditions, and post-synthesis rinsing were systematically varied to examine their effect on the shape and dimensionality of the resulting nanostructures, without the use of complex fabrication techniques.

1.4 Significance

This research demonstrates that morphology control does not require complex templating methods, expensive equipment, or advanced nanofabrication facilities. Instead, it establishes

a cost-effective and practical approach that is accessible for broader implementation. High-quality nanostructures are synthesized using simple and affordable laboratory setups, without the need for templates, surfactants, or structure-directing agents. Furthermore, the approach shows potential for scalability, indicating its applicability to larger-scale synthesis for practical and commercial applications.

2. Materials and Methods

2.1 Materials

Potassium permanganate (KMnO_4 , 99.9%, Sigma-Aldrich, Korea); Concentrated hydrochloric acid (HCl , 35-37%, Daejung Pure Chemicals Co. Ltd., Korea); Deionized (DI) water; Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 94%, Duskan Pure Chemical Co. Ltd., Korea).

2.2 Fabrication Technique

Two types of manufactured nanomaterials were studied; [1] Nanodots (0D): These spherical nanoparticles have isotropic properties and high surface energy, making them effective for rapid redox reactions; and [2] Nanorods (1D): These elongated structures facilitate directional electron transport and enhance conductivity in supercapacitor electrodes. Each morphology presents unique advantages that can be tailored to specific applications by controlling their synthesis routes. A low-cost, simple, and scalable wet-chemical fabrication process was explored to synthesize the two forms of nanomaterials. By fine-tuning synthesis conditions, particularly ion

concentration, and rinsing steps, predominantly nanoparticles and nanorods were produced.

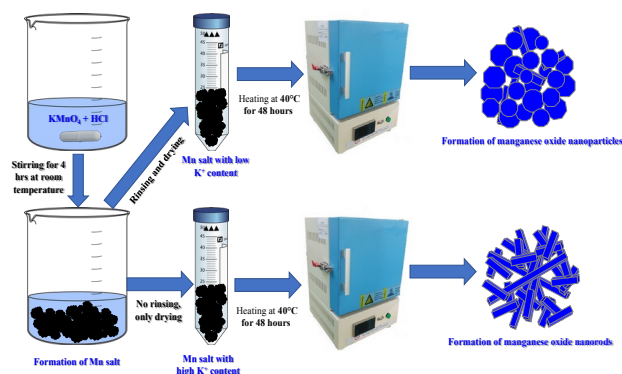
2.3 Method of synthesis

2.3.1 Preparation of HCl solutions

Diluted hydrochloric acid (HCl) solutions of varying concentrations (6M, 4M, and 2M) were prepared prior to synthesis. For each concentration, 30 mL of the respective HCl solution was mixed with 60 mL of distilled water to ensure safe handling and uniform dilution. Distilled water (60 mL) was first added to a clean beaker placed on a magnetic stirrer, and a magnetic stir bar was introduced to ensure continuous mixing. The HCl solution was then added dropwise under stirring to promote gradual mixing and minimize localized concentration gradients. The resulting solution was stirred for an additional 30 minutes to ensure homogeneity.

2.3.2 Manganese oxide synthesis

Manganese oxide nanostructures were synthesized using potassium permanganate (KMnO_4) as the precursor. Initially, 3.16 g of KMnO_4 was dissolved in 80 mL of deionized water under magnetic stirring for 10 minutes to ensure complete dissolution. Subsequently, 20 mL of the prepared HCl solution (6M, 4M, or 2M) was added dropwise to the KMnO_4 solution under continuous stirring. The reaction mixture was then maintained under stirring at room temperature for 4 hours. Following the reaction, two parallel sample batches were prepared under identical conditions: one designated for post-synthesis rinsing and the other for direct drying without rinsing.



Scheme 1. Schematic diagram of the synthesis process.

2.3.3 Post-reaction processing

The reaction mixtures were transferred into centrifuge tubes and balanced with counterweight tubes containing deionized water. The samples were centrifuged multiple times, with the supernatant discarded after each cycle, until a visible solid precipitate was obtained. For non-rinsed samples, the collected solid was directly dried at 40 °C for 48 hours. For rinsed samples, the precipitate was first resuspended in deionized water using a vortex mixer and centrifuged again. This was followed by washing with ethanol, mixing, and subsequent centrifugation. The rinsing procedure using both deionized water and ethanol was repeated five times to reduce residual ionic species. The final product was then dried at 40 °C for 48 hours.

The entire synthesis procedure was repeated for each HCl concentration (6M, 4M, and 2M), while maintaining constant KMnO_4 mass and solvent volume. Unless otherwise specified, all experiments were conducted at ambient laboratory conditions (~25 °C). A schematic

overview of the synthesis process is provided in Scheme 1.

2.4 Characterization

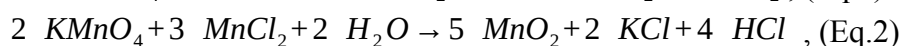
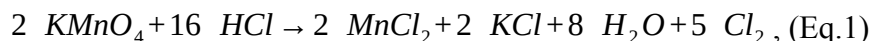
2.4.1 X-Ray Diffraction (XRD) analysis

Phase identification and crystallographic analysis of the synthesized Manganese Oxide samples were performed using X-ray diffraction spectroscopy (XRD). The measurements were conducted on a D8 Advance diffractometer (Bruker, Germany), operated at an accelerating voltage of 40 kV and a cathode current of 30 mA. A Cu K_α radiation source with a wavelength of $\lambda = 1.5406 \text{ \AA}$ was used. To investigate the crystalline structure and phase evolution, diffraction data were collected over a 2θ range of 10° to 90° , with a step size of 0.02° using a PANalytical X'Pert Pro setup. The basic principle of an XRD instrument is discussed in Appendix A of Supplementary materials.

2.4.2 Field-Emission Scanning Electron Microscopy (FE-SEM)

The morphological characteristics and elemental composition of the electrode materials were examined using field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan). For enhanced surface conductivity and image clarity, an ultrathin platinum layer was sputter-coated onto the sample surfaces prior to imaging. The sputter-coating was performed using an ion sputter coater (E-1030, Hitachi, Japan). Elemental analysis was performed using an Energy Dispersive X-ray (EDX) detector column integrated with the FE-SEM instrument, enabling qualitative mapping of elemental distribution across the sample surface. It should be noted that the observed elemental composition is used as a semi-quantitative trend indicator to propose a growth model. The basic principle of an FE-SEM instrument is discussed in Appendix B of Supplementary materials.

3. Chemical analysis



As a result, Equations (1)–(3) represent interdependent pathways within a dynamic reaction environment, rather than a stepwise transformation. The formation of MnO_2 is therefore controlled by the balance between Mn^{2+} generation, Mn^{2+} stabilization in acidic media, and the kinetics of solid-phase nucleation. These factors collectively

The formation of manganese oxide occurs through an acidic reduction of potassium permanganate (KMnO_4), resulting in the formation of Mn(II) salts, as described below. The reaction proceeds through a coupled redox network in which permanganate (MnO_4^-) is partially reduced to Mn^{2+} while simultaneously undergoing comproportionation with Mn^{2+} to form MnO_2 (as shown in Eq. 1-3). These processes occur concurrently, with the relative contributions governed by local acidity and reactant availability. Equations (1)–(3) do not represent a sequential reaction pathway but rather parallel and interdependent processes occurring within the same reaction environment. The formation of MnO_2 is thus governed by the relative kinetics and thermodynamics of these simultaneously occurring reactions (1)–(3), which in turn influence local supersaturation and nucleation kinetics, rather than by a discrete stepwise transformation or transformations (26).

determine local supersaturation, which in turn governs nucleation and growth behavior.

Under highly HCl -rich conditions approaching the stoichiometric ratio of $\text{KMnO}_4:\text{HCl} = 1:8$, the reaction network is dominated by direct reduction of permanganate to Mn^{2+} (Eq. 1). In this regime, Mn^{2+} is strongly stabilized by the acidic environment, which reduces the relative

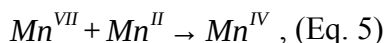
contribution of MnO₂-forming pathways such as comproportionation (Eq. 2). Although these pathways are not completely suppressed, their contribution becomes less significant under strongly acidic conditions.

In contrast, under the present experimental conditions [KMnO₄:HCl = 1:2 (weakly acidic), 1:4 (moderately acidic), and 1:6 (borderline acidic)], the reduction and MnO₂-forming pathways proceed concurrently, with their relative contributions governed by the extent of Mn²⁺ generation and stabilization. At low HCl concentration (1:2), limited proton availability restricts permanganate reduction, resulting in lower Mn²⁺ generation and consequently reduced MnO₂ formation. At intermediate HCl concentrations (1:4–1:6), increased Mn²⁺ generation enhances the likelihood of MnO₂ formation through parallel pathways, while Mn²⁺ remains only partially stabilized. This

balance enables more effective MnO₂ formation.

Therefore, MnO₂ formation may not vary monotonically with acidity, but instead reflects a competition between Mn²⁺ generation (favored by higher acidity) and Mn²⁺ stabilization (also favored by higher acidity). As a result, MnO₂ formation is expected to be maximized within an intermediate acidity regime rather than at either extreme.

Under conditions of limited acidity, permanganate may also undergo direct reduction to MnO₂ (Eq. 4), and in the presence of Mn²⁺, comproportionation reactions (Eq. 5) further contribute to MnO₂ formation. As proton concentration decreases (i.e., as pH increases), the stability of Mn²⁺ is reduced, which can increase the relative contribution of these MnO₂-forming pathways, provided that sufficient Mn²⁺ is available.



In all reactions, potassium ions (K⁺) remain present in the system. Their concentration was controlled indirectly through HCl concentration and post-synthesis rinsing steps. While previous studies suggest that residual K⁺ ions may influence morphology, their role in the present system is interpreted as secondary and correlative, as K⁺ concentration is not independently varied from other chemical parameters such as ionic strength and chloride concentration.

It has been reported that the presence of residual K⁺ ions affects the morphology of the manganese oxide nanostructures (24, 25). To investigate this phenomenon, 2 batches of samples were synthesized, one without rinsing (high K⁺ ion concentration) and another with several rinsing steps (minimum K⁺ ion concentration), to observe its possible effect on the morphological transformation of the manganese oxide nanomaterials.

3.1 K⁺ concentration control strategy

To investigate this effect, two key K⁺ ion concentration control strategies were implemented:

3.1.1 Variation of HCl molarity

The molar concentration of hydrochloric acid was altered across three levels: 6 M, 4 M, and 2 M. This adjustment allowed modulation of the redox environment and indirectly influenced the residual K⁺ ion concentration.

3.1.2 Rinsing (R) vs. Non-Rinsing (NR) treatments

For each molar concentration of HCl, two types of treatments were performed; [1] Rinsing - Multiple centrifugation and wash cycles using DI water and ethanol to minimize K⁺ ion concentration; and [2] Non-Rinsing (NR) - Minimal washing steps to preserve a higher K⁺ ion concentration. The following nomenclature was used to designate sample types as shown in Table 1.

Table 1. Sample nomenclature

Sample Label	HCl Molarity	Rinsing Status
6M-R	6 M	Rinsed
6M-NR		Non-rinsed
4M-R	4 M	Rinsed
4M-NR		Non-rinsed
2M-R	2 M	Rinsed
2M-NR		Non-rinsed

3.2 Comparison strategy

The analysis of chemical composition and nanostructure morphology was conducted in two ways; [1] Within-Molarity Comparison: For example, samples 6M-NR and 6M-R were compared to observe the effect of rinsing at a constant HCl concentration and [2] Across-Molarity Comparison. For example, all non-rinsed samples (6M-NR, 4M-NR, 2M-NR) were compared to observe the effect of decreasing HCl molarity. Similarly, comparing all rinsed samples (6M-R, 4M-R, 2M-R) were also compared to track the morphological evolution under minimized K⁺ conditions.

To assess the reliability of the experimental results, synthesis experiments were repeated under identical conditions, with each replicate corresponding to an independently prepared sample. The reported “Scan-1” and “Scan-2” therefore represent characterization results obtained from separate synthesis runs rather than repeated measurements on the same specimen. Across these independent replicates, consistent trends in yield, phase composition, morphology, and elemental distribution were observed, indicating good repeatability of the synthesis process. The synthesis yield showed low variation between independent runs, with relative differences below 5% under identical conditions. Given the limited number of replicates (n = 2), statistical analyses such as confidence intervals or hypothesis testing were

4. Repeatability and Limitations

4.1 Repeatability

not applied. Instead, repeatability was assessed based on relative variation between independent synthesis runs.

Characterization measurements were also performed on multiple regions and across independently synthesized samples to minimize pseudoreplication. XRD patterns exhibited consistent peak positions and similar relative intensities across replicates, indicating reproducible phase composition. FE-SEM imaging revealed comparable morphological features both within individual samples and across independent syntheses. EDX measurements showed broadly consistent elemental trends, particularly with respect to relative potassium content, although these results are interpreted as semi-quantitative. Overall, the agreement between independent synthesis replicates and multi-region characterization supported the reproducibility of the experimental observations within the scope of the present study.

4.2 Limitations

While this study successfully demonstrated morphology control of manganese oxide nanomaterials, several limitations should be noted.

The potassium (K^+) content was controlled indirectly through synthesis conditions and post-synthesis rinsing, rather than being quantitatively measured using advanced analytical techniques such as X-ray photoelectron spectroscopy (XPS). Energy-dispersive X-ray spectroscopy (EDX) provides only semi-quantitative elemental analysis and

does not yield reliable absolute concentrations of K^+ . Therefore, the EDX results are interpreted as indicative of relative trends and are used for qualitative comparison rather than precise quantification.

The characterization methods used in this work focused on the final structure and composition of the materials. The real-time growth process of the nanostructures was not observed, which limits a detailed understanding of the formation mechanism. Therefore, the formation mechanism is a qualitative model-driven interpretation rather than data-driven.

This study did not include electrochemical testing (CV, GCD, EIS) with proper controls, as the functional testing was outside the scope of the present study. Hence, the functional performance of the materials in energy storage applications was not evaluated. Future studies could address these limitations by incorporating more precise ion analysis, *in situ* characterization, and performance testing.

Advanced statistical tests typically require many repeated experiments and large datasets. In this study, reproducibility was assessed through repeated syntheses, multi-sample measurements, and consistent experimental trends, and basic statistics such as mean and standard deviation were reported where appropriate. More complex statistical analysis was not performed due to the limited number of repeats.

At low HCl concentration (2M), the acidic reduction of $KMnO_4$ becomes reaction-limited,

resulting in incomplete consumption of the permanganate precursor. The unreacted KMnO_4 is subsequently removed during post-synthesis processing, leading to precursor wastage. While this approach enables controlled suppression of MnO_2 formation and nanorod growth, it reduces precursor utilization efficiency and limits direct scalability. Future optimization should focus on minimizing unreacted permanganate or implementing precursor recycling strategies.

This study compares rinsed and non-rinsed samples synthesized at different HCl molarities and therefore does not fully isolate the effects of individual chemical variables. In particular, K^+ , Cl^- , and ionic strength cannot be decoupled, which means, the roles of K^+ ions, Cl^- concentration, and ionic strength cannot be completely separated within the current experimental design. Hence, the observed morphology evolution cannot be uniquely attributed to K^+ ions and may reflect a coupled effect of ionic strength, chloride coordination, and supersaturation kinetics and may hence reflect a global shift in growth regime.

The experimental design in this study was intentionally simple and focused on demonstrating morphology trends rather than providing full quantitative optimization. As a result, parameters such as pH, chloride concentration, and ionic strength were not independently measured or controlled, and K^+ content was inferred rather than quantified using techniques such as ICP-OES or XPS.

In addition, detailed quantitative analyses, including Rietveld refinement and surface area measurements, were not performed. More comprehensive experimental designs, including factorial control of ion chemistry and advanced statistical analysis, are therefore identified as important directions for future work.

5. Results

5.1 Crystallographic properties

The crystallographic characteristics of the synthesized samples were examined using X-ray diffraction (XRD), and the corresponding diffraction patterns are presented in Figure 1. Figure 1(a) compares the XRD patterns of the non-rinsed samples (6M-NR, 4M-NR, and 2M-NR). Diffraction peaks observed at approximately 12.2° , 37.5° , and 67.3° can be indexed to the (110), (211), and (514) planes of MnO_2 , respectively, in agreement with JCPDS-ICDD File No. 44-141. Additional peaks at 22.8° and 52.8° correspond to the (211) and (440) planes of Mn_2O_3 (JCPDS-ICDD File No. 41-1442). These results indicate that both MnO_2 and Mn_2O_3 phases are present in the synthesized materials, consistent with the reaction pathways described in Equations (1)–(3).

Figure 1(b) presents the XRD patterns of the rinsed samples (6M-R, 4M-R, and 2M-R). Similar diffraction features are observed, with peaks corresponding to MnO_2 and Mn_2O_3 appearing at comparable positions (e.g., $\sim 12.6^\circ$, 37.1° , and 66.6° for MnO_2 , and $\sim 24.4^\circ$ and 55.0° for Mn_2O_3). The presence of these peaks across all samples indicates that rinsing

does not significantly alter the phase composition, and that mixed-phase $\text{MnO}_2/\text{Mn}_2\text{O}_3$ structures are consistently obtained under all synthesis conditions.

Qualitative comparison of peak intensities suggests that samples prepared at higher HCl concentration (e.g., 6M) exhibit relatively stronger diffraction peaks. While this may indicate an apparent increase in crystallinity, such comparisons should be interpreted with caution, as peak intensity can also be influenced by factors such as sample packing, preferred orientation, and measurement conditions.

A direct comparison between rinsed and non-rinsed samples at fixed HCl concentrations (Figures 2a–c) shows similar peak positions and overall diffraction profiles, indicating that

rinsing does not produce a substantial change in crystallographic structure. This suggests that the primary phase composition is governed by reaction conditions, while post-synthesis processing has a more limited influence on crystallographic features.

To assess repeatability, XRD measurements were performed on independently synthesized duplicate samples. The peak position and full width at half maximum (FWHM) of the MnO_2 (211) reflection are summarized in Table 2. The results show good agreement between duplicate measurements, with small variations in peak position ($\leq 0.06^\circ$ for $n = 2$) and relatively consistent FWHM values across samples. These observations indicate reasonable reproducibility of the synthesis and characterization.

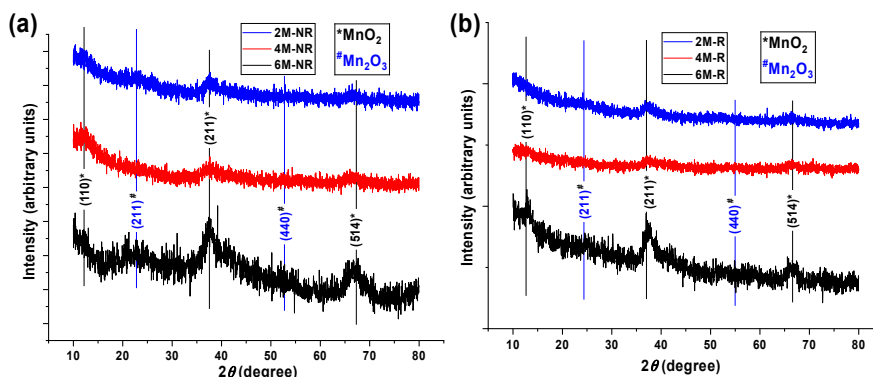


Figure 1(a-b). XRD graphs of non-rinsing and rinsing samples.

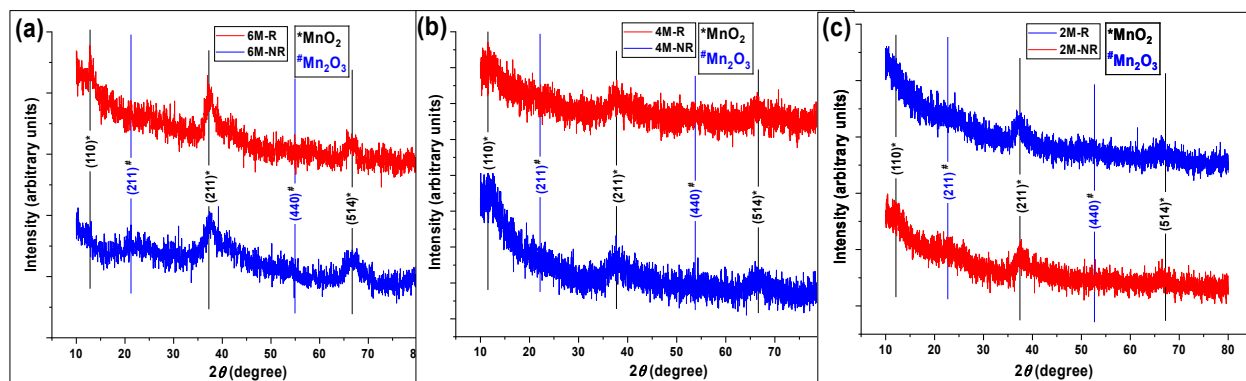


Figure 2(a-c). Comparison of the XRD graphs of non-rinsing and rinsing samples across HCl concentrations.

The average crystallite size was estimated using the Scherrer equation, $D = \beta \cos \theta / K \lambda$, where D is the crystallite size, K is the shape factor (typically 0.94), λ is the X-ray wavelength (0.15406 nm for Cu K α radiation), β is the FWHM in radians, and θ is the Bragg angle of the selected peak. The estimated crystallite sizes range from approximately 3 to 5 nm, indicating the nanostructured nature of the materials. These values should be considered approximate, as instrumental broadening and other sources of peak broadening were not explicitly corrected.

Table 2. XRD peak analysis for (211) MnO₂ peaks of duplicate samples.

Sample	# of Scans	Peak position (deg.)	Mean Peak Position (deg.)	SD Peak Position (deg.)	Peak width (FWHM) (deg.)	Mean FWHM (deg./rad.)	SD of FWHM (deg./rad.)	Avg. crystallite size (nm)
6M-NR	Scan 1	37.56	37.54	0.03	3.20	3.13/0.055	0.11/0.002	3.32 ± 0.12
	Scan 2	37.52			3.05			
6M-R	Scan 1	37.16	37.12	0.06	2.48	2.44/0.043	0.06/0.001	4.22 ± 0.09
	Scan 2	37.07			2.40			
4M-NR	Scan 1	37.54	37.58	0.06	2.16	2.16/0.038	0.01/0.0002	4.81 ± 0.03
	Scan 2	37.62			2.15			
4M-R	Scan 1	37.22	37.26	0.06	3.09	2.95/0.051	0.20/0.003	3.57 ± 0.20
	Scan 2	37.30			2.81			
2M-NR	Scan 1	37.53	37.50	0.04	2.58	2.59/0.045	0.01/0.0002	4.06 ± 0.02
	Scan 2	37.47			2.59			
2M-R	Scan 1	36.77	36.81	0.05	2.15	2.20/0.038	0.07/0.001	4.76 ± 0.12
	Scan 2	36.84			2.25			

5.2 Morphological properties

The surface morphologies of all samples using

FE-SEM, are shown in Figure 3.

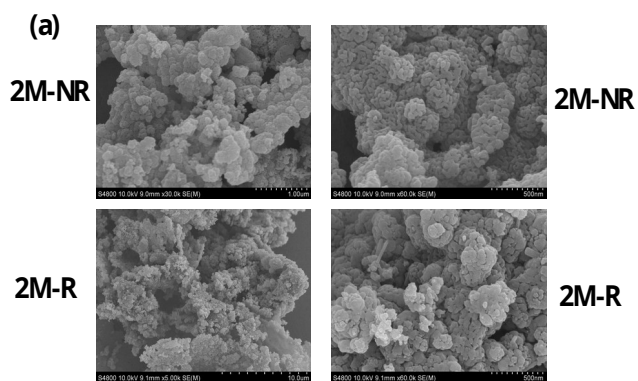


Figure 3(a). FE-SEM images of 2M-NR and 2M-R samples.

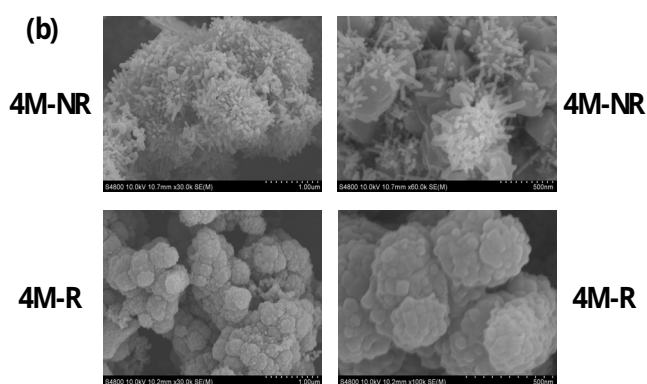


Figure 3(b). FE-SEM images of 4M-NR and 4M-R samples.

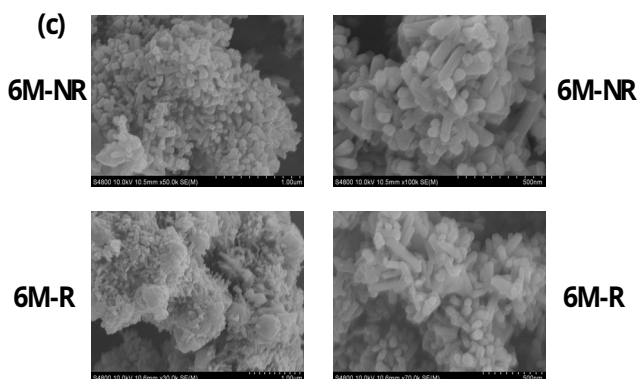


Figure 3(c). FE-SEM images of 6M-NR and 6M-R samples.

Figure 3(a) shows the surface morphologies of 2M-NR and 2M-R at two different magnifications. In the 2M-NR sample, worm-like particles are visible, while in the 2M-R sample, the majority of structures exhibit a near-spherical morphology. Figure 3(b) illustrates the surface morphologies of 4M-NR and 4M-R at two magnifications. The 4M-NR sample shows a mixture of nanorods and nanoparticles, whereas the 4M-R sample predominantly consists of nanoparticles. Figure 3(c) presents the surface morphologies of 6M-NR and 6M-R samples. The 6M-NR sample features exclusively nanorod structures, while the 6M-R sample displays a hybrid morphology containing both nanoparticles and nanorods.

Figure 3(d) compares the morphologies of all six samples at the same magnification. Across the studied range of HCl concentrations, a progressive shift from predominantly nanoparticle morphologies (2M) to mixed structures (4M) and nanorod-dominated morphologies (6M) is observed. This transformation is more pronounced in non-rinsed samples, suggesting that residual ionic species may influence the growth process. The mechanistic origin of this behavior is discussed below.

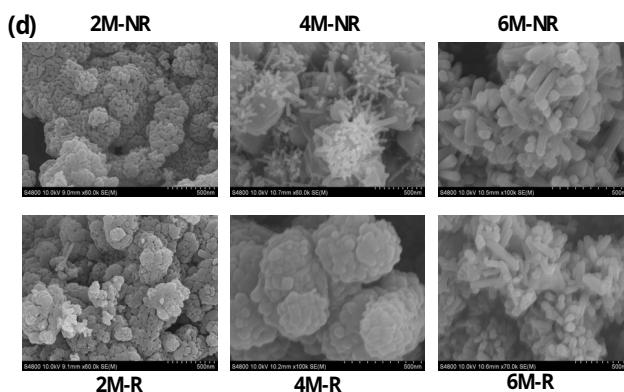


Figure 3(d). Morphologies of all 6 samples are compared at the same magnification.

The observed morphological evolution can be understood in the context of the reaction-driven growth regime described in the chemical analysis section. At low HCl concentration (2M), limited Mn^{2+} generation restricts MnO_2 formation, resulting in low supersaturation and favoring isotropic nucleation and growth, which produces predominantly nanoparticle morphologies.

At intermediate HCl concentration (4M), increased Mn^{2+} availability enhances MnO_2 formation, leading to higher supersaturation and enabling the onset of anisotropic growth. This results in a mixed morphology consisting of both nanoparticles and nanorods. At higher HCl concentration (6M), within the studied range, Mn^{2+} generation is further increased while not being fully stabilized, leading to the highest effective MnO_2 supersaturation among

the tested conditions. This promotes preferential growth along specific crystallographic directions, resulting in dominant nanorod formation.

Importantly, this trend should not be interpreted as strictly monotonic with acidity

but rather as part of a broader non-linear dependence, where anisotropic growth is maximized within an intermediate regime defined by a balance between Mn^{2+} generation and stabilization.

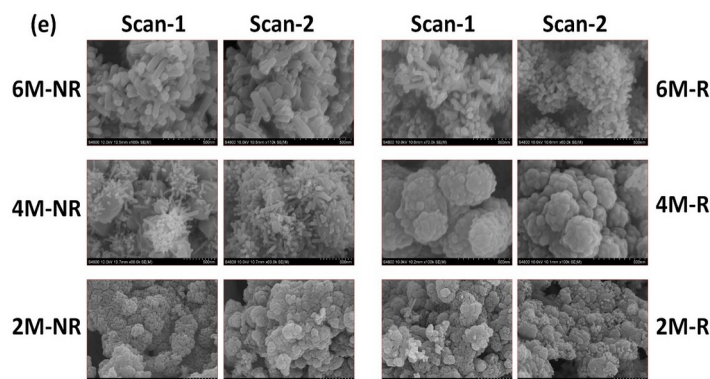


Figure 3(e). Morphology of each sample with duplicate synthesis (Scan-1 & Scan-2).

To assess the repeatability of the experiment, repeat scans were performed independently on duplicate samples, as shown in Figure 3(e). Duplicate samples, fabricated under similar synthesis conditions, show near-identical morphology, indicating good repeatability and process stability.

Column charts of length- and width-distributions of nanorod dimensions for 4M-NR and 6M-NR samples are shown in Fig. 4(a) and (b), respectively. The data were collected from the corresponding FE-SEM images (scan-1 of Figure 3e for 6M-NR and scan-2 of Figure 3e for 4M-NR), using some image

analysis software. Around 95-110 nanorods were counted per distribution. Further analyses of the data through Gaussian fitting reveal an average nanorod length / width (mean $\pm$ SD) of 4M-NR and 6M-NR around 108.6 ± 5.8 / 34.1 ± 1.28 nm and 151.7 ± 7.7 / 41.4 ± 0.75 nm, respectively. The average aspect ratios (length/width) are observed to be around 3.3 and 3.7 for 4M-NR and 6M-NR samples, respectively. An increase in the average length and width for the latter sample is observed, the reason of which is discussed later. For duplicate samples, the difference in the average nanorod length/width is less than 5%, indicating high repeatability.

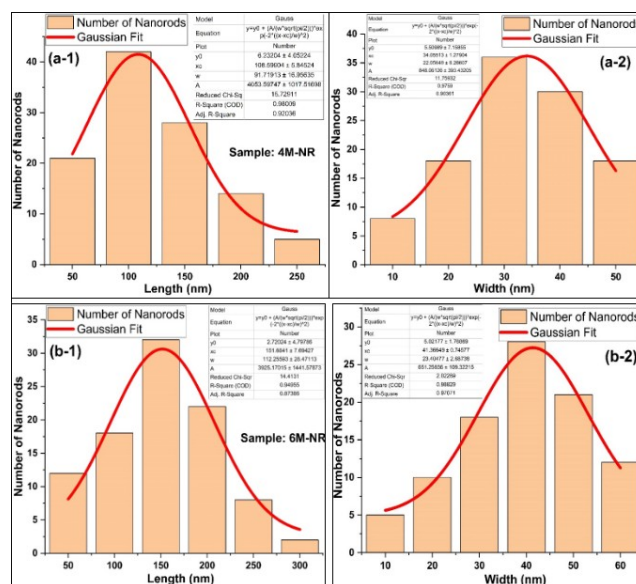


Figure 4. Distribution of nanorod lengths (a-1/b-1) and nanorod widths (a-2/b-2) for 4M-NR and 6M-NR samples.

5.3 Compositional analysis

The chemical composition of all samples was estimated through EDX analysis, using the FE-SEM instrument. Results are shown in Figure 5. In Figure 5(a–c), the left panels present the EDX spectra, the center images indicate the

analyzed regions, and the right panels summarize the corresponding elemental compositions derived from EDX measurements. As expected, Mn, K, and O are detected in all samples.

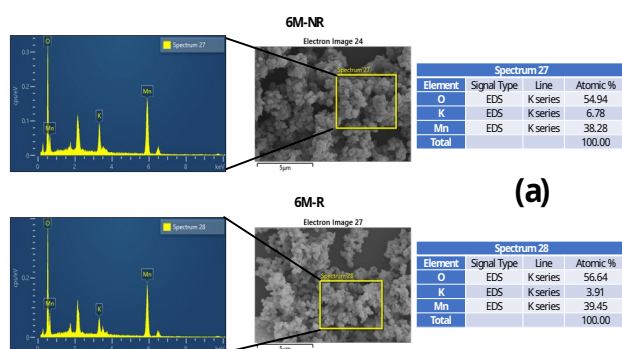


Figure 5(a). EDX analysis of 6M-NR and 6M-R samples.

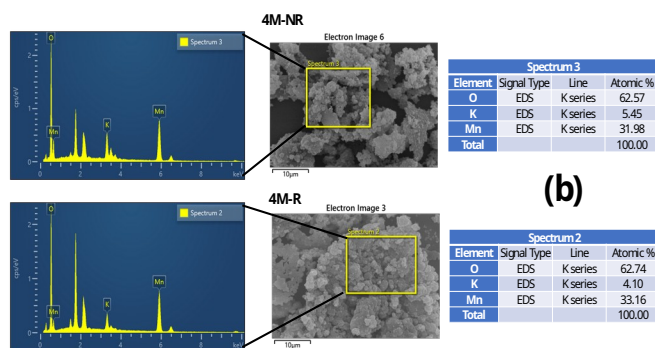


Figure 5(b). EDX analysis of 4M-NR and 4M-R samples.

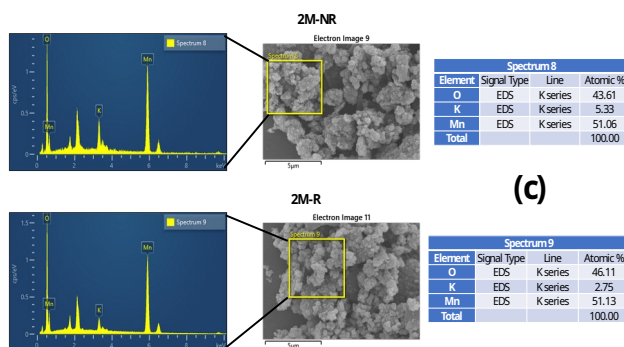


Figure 5(c). EDX analysis of 2M-NR and 2M-R samples.

A qualitative decrease in K atomic percentage is observed following rinsing. For example, in the 6M samples, the K content decreases from 6.78 at% in the non-rinsed sample (6M-NR) to 3.91 at% in the rinsed sample (6M-R) (Figure 5a). A similar trend is observed for the 4M samples, where K content decreases from 5.45 at% to 4.10 at% upon rinsing (Figure 5b), and for the 2M samples, where it decreases from 5.33 at% to 2.75 at% (Figure 5c). These values are interpreted as semi-quantitative indicators of relative elemental composition, and the observed changes are best understood as qualitative trends rather than precise quantitative differences. To better visualize the

trend in K% across all samples, a summary is provided in Table 3.

The EDX results indicate a general reduction in residual K content following rinsing, with non-rinsed samples consistently exhibiting higher average K atomic percentages than their rinsed counterparts. Across non-rinsed samples, a qualitative trend of decreasing K content with decreasing HCl concentration ($6M > 4M > 2M$) is observed. In contrast, this trend is less clearly resolved in rinsed samples due to greater variability between measurements, as reflected in the larger standard deviations. In particular, the overlap in K atomic percentages between 6M-R and 4M-R suggests that

differences between these samples cannot be considered statistically significant based on the present data.

Table 3. Variation of K% across samples.

Sample	K (at%) — Scan 1	K (at%) — Scan 2	Mean K (at%)	SD (at%)
6M-NR	6.78	7.41	7.10	0.45
4M-NR	5.45	5.99	5.72	0.38
2M-NR	5.33	5.45	5.39	0.09
6M-R	3.91	5.21	4.56	0.92
4M-R	4.10	4.96	4.53	0.61
2M-R	2.75	4.10	3.43	0.96

It should be noted that EDX provides semi-quantitative elemental analysis and does not directly measure ionic concentration or oxidation state. Furthermore, the limited number of measurements ($n = 2$) restricts statistical interpretation. Therefore, the reported K atomic percentages are best understood as indicative of relative trends rather than precise quantitative values. Within this context, the results support the interpretation that residual K-containing species are reduced through rinsing and vary qualitatively with synthesis conditions. However, their role in morphology evolution is considered secondary and correlative, as K content cannot be independently varied from other coupled parameters such as ionic strength and chloride concentration. The EDX results qualitatively indicate that residual K-containing species can be influenced through variation of synthesis conditions and post-synthesis processing. In particular, decreasing HCl concentration and applying rinsing steps are associated with a reduction in the measured K atomic percentage, suggesting that these

parameters provide indirect control over residual ionic content within the samples.

The relationship between K content and morphology is examined in conjunction with the observed structural evolution. As shown in Figure 3, a transition from nanoparticle-dominated to nanorod-rich morphologies is observed across the studied conditions. While this trend coincides with variations in residual K content, it should be interpreted within the broader context of the chemically defined growth regime. In this framework, K-containing species may contribute to anisotropic growth as secondary, growth-modifying factors, but the observed morphology evolution cannot be attributed to K content alone. The underlying mechanistic interpretation is discussed in the following section.

6. Discussion

Based on Equations (1)–(3), Table 3, and Figures 1–5, the results indicate that HCl stoichiometry plays an important role in

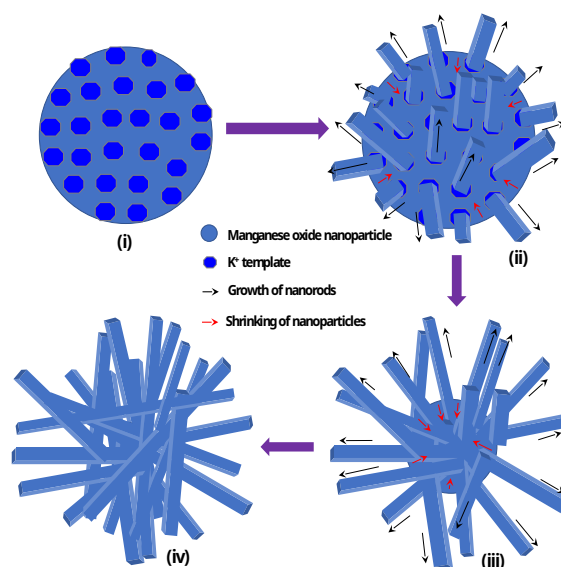
controlling MnO_2 availability and overall structure, while K^+ ions contribute by promoting directional growth of the manganese oxide nanostructures. Overall, the observed morphology evolution reflects a growth environment primarily defined by reaction stoichiometry, with residual K^+ ions contributing to anisotropic development in a qualitative manner. This anisotropic growth is likely governed by kinetic factors, where differential growth rates along specific crystallographic directions under supersaturated conditions favor one-dimensional nanorod formation. The role of K^+ is therefore interpreted as associative rather than quantitatively resolved, and alternative contributions from coupled factors such as ionic strength and chloride chemistry cannot be ruled out.

The observed crystallographic and morphological evolutions of manganese oxide nanostructures are mostly governed by the stoichiometry of HCl in the acidic reduction of KMnO_4 . Because the balanced reaction (Eq. 1) requires a 1:8 KMnO_4 : HCl ratio, the lower ratios used in this study (1:2, 1:4, and 1:6) make HCl the limiting reactant. As a result, decreasing HCl molarity reduces the generation of Mn^{2+} (MnCl_2), which in turn limits MnO_2 formation (Eq. 2) and lowers supersaturation in the reaction system. Under these conditions, nanorod growth is suppressed and nanoparticle-dominated morphologies are favored. Within this HCl -controlled supersaturation regime, residual K^+ ions act as secondary growth-directing species, biasing crystal growth toward one-dimensional nanorod structures when

sufficient MnO_2 is available. Thus, morphology control in this system arises from the combined effects of HCl stoichiometry-driven MnO_2 availability and K^+ -assisted directional growth. In other words, reaction stoichiometry establishes the dominant growth conditions, while residual K^+ ions are associated with differences in the degree of anisotropic structural development.

Within the present synthesis conditions, primarily governed by HCl -controlled reaction chemistry, residual K^+ -containing species are considered as potential secondary growth-modifying factors during the post-synthesis processing stage. When sufficient MnO_2 is available, the presence of K^+ may contribute to the transformation of initially amorphous manganese oxide into mixed MnO_2 and Mn_2O_3 phases (Eq. 3), and may influence the development of anisotropic, one-dimensional nanostructures. A qualitative association between higher retained K content and increased extent of nanorod formation is observed within the studied conditions.

It is hypothesized that K^+ ions may partially occupy interlayer or tunnel sites within the manganese oxide framework, potentially influencing crystal growth behavior and contributing to directional growth. A schematic representation of the proposed nanoparticle-to-nanorod transformation is shown in Scheme 2. However, this interpretation remains a working hypothesis based on qualitative observations, and does not establish a direct causal role for K^+ in morphology evolution.



Scheme-2. Schematic diagram of nanoparticle-to-nanorod formation process.

The crystallization process can be interpreted in terms of two coupled stages within the HCl-controlled reaction environment: nucleation and growth. These stages occur concurrently and are governed by the balance between Mn^{2+} generation, Mn^{2+} stabilization, and the resulting MnO_2 supersaturation.

During the initial nucleation stage, the formation of manganese oxide nuclei is influenced by local supersaturation conditions rather than by a single directing species. Under the studied conditions, higher HCl concentrations promote increased Mn^{2+} generation and subsequent MnO_2 formation, which enhances effective supersaturation and facilitates nucleation. Qualitative differences in XRD peak sharpness and intensity are observed across samples, with those synthesized at higher HCl concentrations (e.g., 6M) exhibiting

more pronounced diffraction features. However, such variations should be interpreted cautiously, as peak intensity may also be influenced by factors such as preferred orientation and sample preparation.

Following nucleation, crystal growth proceeds under conditions where both thermodynamic and kinetic factors influence morphology evolution. Under low HCl concentration (2M), limited Mn^{2+} generation restricts MnO_2 formation and results in lower supersaturation, favoring isotropic growth and the formation of nanoparticle-like or irregular structures (Figure 3a). At intermediate conditions (4M), increased MnO_2 formation leads to higher supersaturation, enabling the onset of anisotropic growth and resulting in mixed morphologies (Figure 3b). At higher HCl concentration within the studied range (6M),

the highest effective supersaturation is achieved, promoting preferential growth along specific crystallographic directions and resulting in dominant nanorod formation (Figure 3c). This anisotropic growth is likely governed by kinetic factors, where differential growth rates along crystallographic directions favor one-dimensional structures under supersaturated conditions.

Post-synthesis rinsing modifies the residual ionic environment and is associated with a

reduction in nanorod formation relative to non-rinsed samples (Figure 3d). This effect is interpreted as a change in the growth environment rather than as evidence of a single controlling variable. In particular, residual K^+ -containing species may act as secondary, growth-modifying factors within the chemically defined regime, although their effects cannot be isolated from concurrent changes in ionic strength and chloride concentration.

Table 4. Effect of $KMnO_4$: HCl molar ratio, K^+ concentration and morphology

$KMnO_4$: HCl molar ratio	Relative acidity regime	Relative Mn^{2+} generation (inferred)	Effective MnO_2 formation tendency (qualitative)	K^+ content trend (EDX, qualitative)	Observed morphology
1 : 2	Low acidity (HCl strongly limiting)	Low (limited reduction)	Low (limited supersaturation)	Lower	Predominantly nanoparticles
1 : 4	Intermediate acidity	Moderate	Moderate (increased supersaturation)	Intermediate	Mixed nanoparticles and nanorods
1 : 6	Upper-intermediate acidity (within studied range)	Higher	Higher effective supersaturation (within studied range)	Higher	Predominantly nanorods

Mn^{2+} generation and MnO_2 formation are inferred qualitatively based on reaction stoichiometry and observed trends, as these quantities were not directly measured. EDX measurements provide only semi-quantitative elemental composition and do not resolve oxidation states or phase fractions. Therefore, the values reported here reflect relative trends rather than absolute quantities.

It is important to note that the reaction system is HCl-limited, particularly at lower $KMnO_4$:HCl ratios. Under these conditions, reduced proton availability limits Mn^{2+} generation and subsequently MnO_2 formation, leading to lower supersaturation and suppressed anisotropic growth. At higher HCl ratios within the studied range, increased Mn^{2+} generation enhances MnO_2 formation and raises effective supersaturation, thereby

enabling nanorod formation. The proposed growth mechanism is qualitative and based on indirect inference from morphology and reaction conditions, and should be interpreted within this context. Table 4 provides a qualitative framework of the stoichiometry and K^+ concentration as they relate to morphology.

6.1 Variations in phase composition

It can be considered that variations in phase composition may influence surface energy, nucleation behavior, and growth anisotropy, and could therefore contribute to the observed nanoparticle-to-nanorod transformation. However, XRD analysis indicates that all samples, irrespective of $\text{KMnO}_4\text{:HCl}$ ratio or rinsing condition, contain both MnO_2 and Mn_2O_3 phases, with no sample exhibiting a phase-pure structure. While minor variations in relative peak intensities are observed across different synthesis conditions, the same characteristic diffraction peaks corresponding to MnO_2 and Mn_2O_3 are consistently present in both nanoparticle-dominated samples (e.g., 2M-R, 2M-NR) and nanorod-dominated samples (e.g., 6M-NR). This suggests that the nanoparticle-to-nanorod transformation does not arise from the emergence or disappearance of a specific crystalline phase.

Furthermore, within a fixed HCl molarity—where the overall reaction environment and phase composition are expected to be comparable—rinsed and non-rinsed samples exhibit distinct morphological differences despite similar XRD phase signatures (Figure 2a–c vs Figure 3d). For instance, at 6M HCl, the relative peak intensity ratio of MnO_2 (211) to Mn_2O_3 (440) is comparable for both non-rinsed and rinsed samples (~ 2.10 and ~ 2.17 , respectively), yet the non-rinsed sample (6M-NR) exhibits predominantly nanorod morphology, whereas the rinsed sample (6M-R) shows a mixed morphology. Similarly, at 4M HCl, nearly identical intensity ratios (~ 1.50 and ~ 1.51) are observed for non-rinsed and

rinsed samples, while 4M-NR exhibits mixed nanorod structures and 4M-R remains predominantly nanoparticulate.

These observations indicate that morphology cannot be attributed solely to phase composition. Instead, phase composition appears to define a broader growth regime, within which additional factors influence the resulting morphology. In particular, variations in residual ionic species, such as K^+ , may modulate anisotropic growth behavior within this regime, although their effects cannot be isolated independently of other coupled parameters such as ionic strength and chloride concentration.

It should be noted that the present analysis is based on qualitative comparison of XRD peak intensities. A more rigorous decoupling of phase composition and ion-mediated growth effects would require quantitative phase analysis (e.g., Rietveld refinement) and independent control of $\text{MnO}_2\text{:Mn}_2\text{O}_3$ ratios, which are beyond the scope of this study (see Limitations section).

6.2 Role of residual KMnO_4

The potential influence of residual KMnO_4 on morphological evolution was considered; however, several observations suggest that it is not the primary factor governing anisotropic nanorod growth. First, XRD patterns of non-rinsed samples do not show detectable diffraction peaks corresponding to crystalline KMnO_4 , indicating that any residual permanganate, if present, exists at low concentration or in an amorphous or highly

dispersed form below the detection limit. Second, within a fixed HCl molarity—where the redox environment during synthesis is comparable—rinsed and non-rinsed samples exhibit distinct morphological differences despite similar XRD phase signatures. This suggests that post-synthesis ionic species, rather than residual oxidant alone, contribute to the observed morphological variations. Furthermore, if residual KMnO_4 were the dominant factor driving anisotropic growth, nanorod formation would be expected whenever unreacted permanganate is present. However, at low HCl molarity (e.g., $\text{KMnO}_4\text{:HCl} = 1\text{:}2$), nanorod formation is suppressed even in non-rinsed samples, where incomplete reaction makes residual KMnO_4 more likely. This indicates that the presence of permanganate alone is insufficient to induce anisotropic growth.

Taken together, these observations suggest that residual KMnO_4 does not independently control morphology, but rather that nanorod formation arises from a combination of reaction-driven supersaturation conditions and ion-mediated growth effects within the chemically defined regime.

6.3 K^+ ion control

Several strategies have been reported for regulating K^+ ion content in manganese oxide systems, including adjusting the initial precursor composition prior to manganese oxide formation, introducing additional alkali ions before heat treatment, and modifying rinsing protocols during post-synthesis processing (27, 43, 44). In the present study, a

two-step approach was adopted to influence the effective K^+ ion content. First, the molar concentration of HCl (6M, 4M, and 2M) was varied to modulate the reaction environment during synthesis, which indirectly affects the incorporation and retention of alkali ions. Second, post-synthesis rinsing steps were applied to selectively reduce residual K^+ ions in the final product.

Together, this combined strategy provides a simple and accessible approach for influencing the formation of manganese oxide nanostructures, particularly the transition toward nanorod morphologies, within the chemically defined growth regime.

6.4 Summary

In summary, the observed evolution of manganese oxide morphology can be understood as a consequence of a chemically defined growth regime governed by the interplay between Mn^{2+} generation, Mn^{2+} stabilization, and the resulting MnO_2 supersaturation. Under low HCl conditions, limited proton availability restricts the reduction of permanganate, leading to reduced Mn^{2+} generation and consequently low MnO_2 formation. This results in low supersaturation, favoring isotropic nucleation and the formation of nanoparticle morphologies. As the HCl concentration increases, enhanced permanganate reduction leads to greater Mn^{2+} availability. Within the studied range, Mn^{2+} is not fully stabilized, allowing MnO_2 -forming pathways such as comproportionation to proceed more effectively. This increases local supersaturation, promoting anisotropic growth

and the formation of nanorod structures. The proposed growth mechanism is qualitative and based on indirect inference from morphology and reaction conditions.

Importantly, this behavior reflects a non-monotonic dependence on acidity. While increasing HCl concentration within the present experimental range (2M–6M) promotes nanorod formation, this trend is expected to reverse at sufficiently high acidity, where strong stabilization of Mn^{2+} suppresses MnO_2 formation. Therefore, the observed morphology evolution represents a partial sampling of a broader growth regime in which anisotropic structures are maximized at intermediate acidity.

In this context, potassium ions (K^+) are interpreted as secondary, growth-modifying species that may influence anisotropic growth within this regime. However, as K^+ concentration is not independently controlled from other chemical parameters such as ionic strength and chloride concentration, its role is considered correlative rather than causative.

7. Conclusion and perspective

This study demonstrates that the morphology of manganese oxide nanostructures can be effectively tuned through simple modifications of reaction stoichiometry and post-synthesis processing conditions. By varying the molar concentration of HCl and applying controlled rinsing procedures, the chemical environment during synthesis and the retention of residual potassium ions (K^+) were systematically altered. These changes resulted in a clear

progression from nanoparticle-dominated to nanorod-rich morphologies across the investigated conditions.

The results suggest that morphology evolution is governed primarily by a growth regime defined by the balance between Mn^{2+} generation, Mn^{2+} stabilization, and the resulting MnO_2 supersaturation. Within the studied range of HCl concentrations, increased acidity enhances Mn^{2+} generation and promotes MnO_2 formation, leading to higher effective supersaturation and the onset of anisotropic growth. This is reflected in the transition from isotropic nanoparticles to one-dimensional nanorod structures. XRD analysis confirms the presence of mixed MnO_2 and Mn_2O_3 phases across all samples, while FE-SEM observations reveal distinct morphology changes. EDX measurements further indicate that rinsing reduces residual potassium content, although these measurements remain semi-quantitative.

Importantly, the observed trends should not be interpreted as strictly monotonic with acidity, but rather as reflecting a broader non-linear dependence in which anisotropic growth is favored within an intermediate regime. Within this framework, residual K^+ ions are interpreted as secondary, growth-modifying species that may influence anisotropy, rather than as primary determinants of phase formation or morphology. Their effects cannot be decoupled from concurrent changes in ionic strength and chloride concentration in the present experimental design.

Overall, this work provides a simple and accessible approach to morphology control in MnOx nanomaterials without the need for templates or advanced fabrication techniques. However, the mechanistic interpretation remains qualitative. Future studies should aim to decouple individual chemical variables through controlled experiments, such as independently varying K^+ concentration (e.g., via KCl addition at fixed acidity), using alternative permanganate precursors, or employing different acids to isolate chloride effects. Additional quantitative analyses, including phase fraction determination and in situ characterization, would further clarify the growth mechanism.

Further work is also needed to evaluate the functional implications of the observed morphologies. Electrochemical testing could

assess their suitability for energy storage applications, while investigations of other alkali ions (e.g., Li^+ , Na^+) may provide additional insight into ion-mediated growth behavior. Studies on long-term structural stability, as well as the development of composite materials and scalable or environmentally benign synthesis routes, would help advance these findings toward practical applications.

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9. Supplementary materials

9.1 Appendix A - X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a technique used to analyze the crystal structure and phase composition of materials. In this study, XRD was used to examine the phase evolution and crystallinity of synthesized manganese oxide samples.

The instrument used was a D8 Advance diffractometer (Bruker, Germany), operated at 40 kV accelerating voltage and 30 mA cathode current. A Cu K α radiation source with a wavelength of $\lambda = 1.5406 \text{ \AA}$ was used to irradiate the sample. The PANalytical X'Pert Pro software collected data over a 2θ range of 10° to 90° , with a step size of 0.02° .

Basic Principle: The XRD machine generates X-rays that strike the sample. When the sample has a crystalline structure, the X-rays diffract at specific angles. This diffraction occurs according to Bragg's Law: $n\lambda = 2d \cdot \sin(\theta)$, where λ = X-ray wavelength, d = distance between atomic layers, θ = diffraction angle and n = order of reflection (usually 1). The detector measures the intensity of these diffracted rays across different angles. The resulting pattern, called a diffractogram, is unique to each material and is used to identify phases and evaluate structural properties.

In this study, XRD was used to confirm the presence of MnO₂ and Mn₂O₃ phases, detect structural differences due to rinsing or acid concentration and estimate crystallinity using peak sharpness and position.

9.2 Appendix B - Field-Emission Scanning Electron Microscope (FE-SEM)

Field-emission scanning electron microscopy (FE-SEM) is a high-resolution imaging technique used to analyze the surface morphology and elemental distribution of materials at the micro- and nano-scale. In this study, FE-SEM (model S-4800, Hitachi, Japan) was used to examine the structure and composition of manganese oxide samples.

Working Principle: The FE-SEM uses a focused beam of high-energy electrons emitted from a field-emission gun (FEG). These electrons interact with atoms on the surface of the sample, producing various signals, including secondary electrons and characteristic X-rays. Secondary electrons provide detailed topographical images, while X-rays are used for elemental analysis. To improve image clarity and prevent charging, a thin platinum coating was applied to the sample surface using an ion sputter coater (E-1030, Hitachi, Japan).

In this study, high-resolution imaging was used to determine the nanostructure and morphology of MnO₂ samples. Elemental analysis was performed using an X-ray detector column attached to the FE-SEM which allowed the spatial visualization of elements such as manganese, oxygen, and potassium across the surface.