Engineering Co$_3$O$_4$/MnO$_2$ nanocomposite materials for oxygen reduction electrocatalysis

Ababay Ketema Worku$^a$, Delele Worku Ayele$^{a, b, *}$, Nigus Gabbiye Habtu$^{a, c, **}$, Temesgen Atnafu Yemata$^c$

$^a$ Bahir Dar Energy Center, Bahir Dar University, P.O. Box 26, Ethiopia  
$^b$ Department of Chemistry, College of Science, Bahir Dar University, P.O. Box 79, Bahir Dar, Ethiopia  
$^c$ Department of Chemical Engineering, Bahir Dar Institute of Technology, Bahir Dar University, P.O. Box 26, Bahir Dar, Ethiopia

**Corresponding author.**  
**Corresponding author.**

E-mail addresses: delelewww@gmail.com (D.W. Ayele), nigushabtu@gmail.com (N.G. Habtu).

HIGHLIGHTS

- Co$_3$O$_4$/MnO$_2$ nanocomposites have been effectively synthesized via a co-precipitation route.
- The addition of Co$_3$O$_4$ in MnO$_2$ led to a drastic change in the electrochemical properties.
- The electrochemical behaviors of Co$_3$O$_4$/MnO$_2$ nanocomposites have been investigated.
- The Co$_3$O$_4$/MnO$_2$ nanocomposite electrode exhibits high stabilities and high catalytic activities.

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ABSTRACT

Stable and active electrocatalysts preparation for the oxygen reduction reaction (ORR) is essential for an energy storage and conversion materials (e.g. metal-air batteries). Herein, we prepared a highly-active MnO$_2$ and Co$_3$O$_4$/MnO$_2$ nanocomposite electrocatalysts using a facial co-precipitation approach. The electrocatalytic activity was examined in alkaline media with LSV and CV. Additionally, the physicochemical characteristics of the MnO$_2$ and Co$_3$O$_4$/MnO$_2$ composite materials were studied via SEM, XRD, BET, UV-Vis, TGA/DTA, ICP-OES and FTIR. Morphological studies indicated that a pure MnO$_2$ has a spherical flower-like architecture, whereas Co$_3$O$_4$/MnO$_2$ nanocomposites have an aggregated needle-like structure. Moreover, from the XRD investigation parameters such as the dislocation density, micro-strain, and crystallite size were analyzed. The calculated energy bandgaps for the MnO$_2$, Co$_3$O$_4$/MnO$_2$-1-5, and Co$_3$O$_4$/MnO$_2$-1-1 nanocomposites were 3.07, 2.6, and 2.3 eV, correspondingly. The FTIR spectroscopy was also employed to study the presence of M-O bonds (M = Mn, Co). The thermal gravimetric investigation showed that the Co$_3$O$_4$/MnO$_2$ nanocomposite materials exhibited improved thermal stability, confirming an enhanced catalytic activity of ORR for MnO$_2$/Co$_3$O$_4$-1-1 composite materials for ORR. These results confirm that the prepared Co$_3$O$_4$/MnO$_2$ composite materials are promising air electrode candidates for the energy storage and conversion technologies.

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1. Introduction

Recently, renewable energy has been regarded as a sustainable approach to overcome current global warming issues [1, 2]. Thus, sustainable and reliable prospects can be achieved by creating novel energy conversion and storage devices [3, 4]. Thus, batteries, supercapacitors, and fuel cells are the most effective technologies for solving these challenges. The oxygen reduction reaction (ORR) is the governing electrochemical reaction in the discharge process, which affects the performance of these devices [5]. However, the ORR suffers from high polarization and sluggish kinetics, which decreases the overall performance of the battery [6, 7]. Hence, different researchers have concentrated on preparing effective, low-cost, and durable oxygen electrocatalysts to significantly enhance the reaction kinetics of the ORR. Recently, different types of electrocatalysts such as precious metals, carbon-derived catalysts, transition-metals, and transition metal oxides (e.g. NiO, CuO, MnO₂, and Co₃O₄) have been reported to overcome the overpotential and improve the cycling performance for ORR purposes [8, 9, 10]. Transition metal oxides are attractive electrocatalysts for the ORR due to their low price, remarkable cycle stability, and environmental friendliness. From them, manganese dioxide (MnO₂) has become the most potential and most attractive material with best electrochemical characteristics due to its excellent specific capacity, high abundance, high specific surface area, eco-friendly, low cost, and boost catalytic activity [11, 12]. However, poor electronic conductivity is one of the opposing outcomes observed when MnO₂ is applied as an electrocatalyst owing to its limited cycle performance [13, 14]. The principal approach for enhancing the performance of MnO₂ is to blend it with conducting materials like oxides, metals, and carbon-derived materials [15, 16]. Spinel Co₃O₄ is an alternative type of electrocatalyst that has low resistivity and excellent ORR catalytic performance [17, 18]. Mixing these two classes of materials provides a nanocomposite material with collaboration and coping effects that create oxygen vacancies, which improves the ORR activity [19, 20]. To enhance the electrochemical performance of the catalysts for ORR, nanocomposite catalysts such as CuO@MnO₂ [21], NiCoO₂@MnO₂ [22], TiO₂@MnO₂ [23], ZnO/MnO₂ [24], Fe₂O₃–MnO₂ [25], Co₃O₄/MnO₂-CNTs [26], and Co₃O₄@MnO₂ [27] have been investigated. The synergetic effect of the individual components allows the nanocomposite structure to exhibit improved characteristics [28]. However, the cost-effective, novel and simple preparation route of MnO₂-based nanocomposites with excellent activity, stability, and durability remains a challenge [29, 30]. Hence, the electrochemical activity of nanocomposites depends on their preparation process because of the essential material characteristics (e.g., porosity, particle size, crystal structure, and morphology), which rely on the development of MnO₂ and Co₃O₄/MnO₂ nanocomposites [31]. Sol-gel, hydrothermal [32, 33], soft template [34, 35], micro-emulsion [36], hummers, and co-precipitation, are common techniques for the preparation of MnO₂ and Co₃O₄/MnO₂ nanocomposites. In contrast to other methods, co-precipitation preparation offers several benefits such as a simple, rapid, and cost-effective method at room temperature under ambient pressure [37]. Despite these advantages, however, studies on the co-precipitation synthesis of MnO₂ and Co₃O₄/MnO₂ nanocomposites are still limited [38, 39, 40]. Recently, nanocomposite metal oxides have gained significant attention. However, only a few studies have been conducted on Co₃O₄/MnO₂ nanocomposites as cathode materials [41, 42]. Moreover, studies on the application of Co₃O₄/MnO₂ nanocomposites as air electrodes remain limited, while the morphology and size of the synthesized materials are expected to affect their characteristics and performance. Herein we report MnO₂ and Co₃O₄/MnO₂ nanocomposites using a template-free, cost-effective, simple, and rapid co-precipitation technique [43].

2. Experimental section

2.1. Chemical and materials

All chemicals employed in this experiment were acquired from commercial dealers of analytical rank and were utilized as received without additional purification. Manganese sulfate monohydrate (99 %, MnSO₄·H₂O, India (Sisco Research Laboratories Pvt. Ltd.)), Cobalt (II) nitrate hexahydrate (99.5%, Co(NO₃)₂·6H₂O) and ammonia (China Sinopharm Chemical Reagent Co., Ltd.). Sodium hydroxide (NaOH, 99.5%), Vulcan XC 72 carbon powder (96.5%), potassium hydroxide (97.5%, KOH), potassium permanganate (99.5%, KMnO₄), ethanol (98.5%), and sodium carbonate (97.5%) were obtained from Alpha Chemika (India). Throughout the experiments distilled water (DW) was employed as the solvent.

2.2. Synthesis of MnO₂ NPs

Nanoparticles (NPs) of MnO₂ were synthesized via a co-precipitation method. In a typical procedure, 5.07g of MnSO₄·H₂O was dissolved in DW (100 mL) with vigorously stirring. Then, 3.16 g of KMnO₄ was dissolved in DW of 100 mL and mixed dropwise to the earlier suspension. The mixture was vigorously stirred at 80 °C for 5 h. While stirring, 0.2 M solution of NaOH was added to adjust the pH of the mixture to be 11. A precipitate of as-prepared MnO₂ was obtained. The precipitant was cleaned with DW and filtered. Finally, the obtained nanoparticles were dried at 100 °C for 6 h.

2.3. Synthesis of Co₃O₄ NPs

Co₃O₄ nanoparticles were prepared via co-precipitation method. In this typical experiment, 4.575 g (0.025M) of Co(NO₃)₂ was dissolved in 100 mL DW, and stirred for 20 min. After stirring, 20 mL sodium carbonate solution (1M) as precipitating agent becomes delivered to the above solution. Then, the mixtures were stirred for 6 h at 60 °C. After 6 h stirring, light purple coloration precipitates were filtered, washed with DW and absolute ethanol, respectively. Then, the final products obtained were dried inside an oven at 80 °C for 12 h. Finally, as prepared catalyst was calcined in an electric furnace for 3 h at 500 °C.

2.4. Synthesis of Co₃O₄/MnO₂ nanocomposites

Co₃O₄/MnO₂ nanocomposites were synthesized using a co-precipitation approach. In a typical synthesis, 0.5 g Co(NO₃)₂·6H₂O was dissolved in 40 mL of DI water followed by mixing of 15 mL of 1.3 M aqua ammonia into the mixture under vigorous stirring condition. The color of the solution was changed to green at first, and was changed to dark green later. Then, 0.125 g of synthesized MnO₂ nanomaterials was dispersed in the above mixture and stirred for 1 h. The synthesized NPs were then filtered and washed with ethanol and DW followed by drying at 80 °C for 10 h to remove water and other organic substances. Lastly, the as-prepared NPs were calcined at 600 °C for 1 h in air. Mn/Co catalysts with various molar ratios (1:5, 1:4, 1:3, 1:2 and 1:1) of the Co₃O₄/MnO₂ catalysts were developed via a similar preparation method. Figure 1 shows detailed of the preparation process of Co₃O₄/MnO₂ nanocomposites via a co-precipitation method. From now onwards MnO₂ was used for pure MnO₂ and Co₃O₄/MnO₂-1-5, Co₃O₄/MnO₂-1-4, Co₃O₄/MnO₂-1-3, Co₃O₄/MnO₂-1-2, and Co₃O₄/MnO₂-1-1 were employed for Co₃O₄/MnO₂ nanocomposites with Co/Mn molar ratios of 1:5, 1:4, 1:3, 1:2 and 1:1 respectively.
2.5. Characterization

Scanning electron microscope (SEM, Inspect™ F50) was employed for morphology study. The XRD profile of developed NPs were examined using X-ray diffraction (XRD) with Cu-Kα radiation (MAXima_X XRD-7000, SHIMADZU) and were measured in 2-theta angle ranging from 10° and 80° at room temperature. FTIR (wavelength range of 400-4000 cm⁻¹, FT-IR 6660, JASCO MODEL) was utilized to examine the functional groups. UV-Vis spectrometer (Lambda 35, PerkinElmer) was utilized to investigate the optical characteristics of the developed NPs. The thermal behavior analysis was accomplished via TGA/DTA technique. Quanta chrome Nova Win (version 11.0) was used to study the surface areas of as-synthesized NPs. The elemental examination was done through inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer 800).

2.6. Electrochemical measurement

For electrochemical measurements a 3-electrode half-cell comprising of glassy carbon electrode (GCE), Ag/AgCl and platinum coil were employed as the working, reference and counter electrodes, respectively. This procedure was used to examine the ORR performance of the MnO₂ and Co₃O₄/MnO₂ nanocomposites in a KOH (0.1 M) aqueous electrolyte. The working electrode has been developed by keeping MnO₂ and Co₃O₄/MnO₂ nanocomposite suspensions on a substrate (glassy carbon). The catalyst suspension was developed by mixing MnO₂ and Co₃O₄/MnO₂ nanocomposites.

![Diagram representation of development of Co₃O₄/MnO₂ nanocomposites via co-precipitation method.](image1)

Figure 1. Diagram representation of development of Co₃O₄/MnO₂ nanocomposites via co-precipitation method.

![XRD profile of (a) MnO₂, (b) Co₃O₄/MnO₂-1-3, (c) Co₃O₄/MnO₂-1-4, (d) Co₃O₄/MnO₂-1-5, (e) Co₃O₄/MnO₂-1-2, (f) Co₃O₄/MnO₂-1-1 nanocomposites.](image2)

Figure 2. XRD profile of (a) MnO₂, (b) Co₃O₄/MnO₂-1-3, (c) Co₃O₄/MnO₂-1-4, (d) Co₃O₄/MnO₂-1-5, (e) Co₃O₄/MnO₂-1-2, (f) Co₃O₄/MnO₂-1-1 nanocomposites.
nanocomposites (5.0 mg) with carbon powder (5.0 mg) to maintain an electronic conductivity in 2.5 ml isopropanol-water solution with 7:3 volume/volume ratios. The catalyst ink was ultrasonically mixed for 10 min and then 8 μL of the prepared suspension was pipetted onto the GCE electrode. Before each measurement (electrochemistry), the electrolyte (KOH, 0.1 M) was saturated by purging high purity oxygen/nitrogen for a minimum of 30 min. The oxygen/nitrogen atmosphere was kept in the electrocatalytic measurements. CHI760E electrochemical workstation was utilized for LSV (5 mV s⁻¹) and CV (5, 10, 20, 50, and 100 mV s⁻¹) measurements in the potential window interval of +0.1 to -0.7 V (vs Ag/AgCl).

3. Results and discussion

3.1. Structural characterization

XRD was conducted to study the crystal structure and composition of the developed nanoparticles over the 2 theta ranges of 10–80 with a scan rate of 0.02°/s. The XRD profile of pure MnO₂ and Co₃O₄/MnO₂ nanocomposites at molar ratios of (1:5, 1:4, 1:3, 1:2 and 1:1) are shown in Figure 2. In the XRD patterns of MnO₂ NPs, the diffraction peaks observed at 37.22°, 42.05°, 66.14°, and 74.45° matched well to the (1 0 0), (1 1 0), and (2 0 0) lattice plane, which are assigned to α-MnO₂ (JCPDS 00-030-0820) diffraction pattern. In the XRD pattern of the Co₃O₄/MnO₂-1-3 hybrid material, the diffraction peaks at 22.38°, 37.42°, 42.69°, and 56.57° correspond to the (101), (210), (211), and (402) crystal planes of γ-MnO₂ (JCPDS No: 14-0644), respectively. The diffraction peaks at 12.60°, 17.95°, 28.99°, and 37.42° (coinciding with γ-MnO₂), 49.94°, 65.62°, and 69.51° were assigned to α-MnO₂ (JCPDS 44-0141), whereas the diffraction peaks at 32.69° and 69.06° assigned to the (220) and (531) crystal planes of Co₃O₄ (JCPDS No: 00-042-1467), respectively [44]. Hence, these indicate that the sample consists of three phases (γ-MnO₂, α-MnO₂ and Co₃O₄). Similarly, the XRD pattern of the Co₃O₄/MnO₂-1-4 nanocomposites showed diffraction peaks at 12.60°, 18.12°, 28.48°, 37.10°, 42.47°, 49.83°, 56.47°, 60.15°, 65.62°, and 72.56° which were assigned to (110), (200), (310), (211), (301), (411), (600), (521), (002), and (312) crystal planes of α-MnO₂ (JCPDS 44-0141), correspondingly; and the diffraction peaks at 32.69° and 69.06° were assigned to the (220) and (531) crystal planes of Co₃O₄ (JCPDS No: 00-042-1467), respectively [44]. The above results confirm the development of the Co₃O₄/MnO₂ nanocomposites. In the XRD profile of Co₃O₄/MnO₂-1-5, Co₃O₄/MnO₂-1-2, and Co₃O₄/MnO₂-1-1 nanocomposites, the diffraction peaks at 28.69°, 37.32°, 42.47°, 56.64°, 59.47°, and 67.41° were matched well to the (110), (101), (111), (211), (220), and (310) lattice plane of β-MnO₂ (JCPDS No: 00-024-0735), respectively [45] and the diffraction peaks at 31.95°, 59.51°, and 65.62° corresponding to the (220), (511), and (440) lattice plane of Co₃O₄ (JCPDS No: 00-043-1003), respectively [46]. Therefore, the samples were included of two phases Co₃O₄ and MnO₂. Therefore, the above results display that the phase of ε-Mn O₂ was transformed into a different structure after the addition of Co₃O₄. As shown in Table 1, the addition of Co₃O₄ affected the basic structure of the ε-Mn O₂ nanocomposites.

### Table 1. Crystallite characteristics and micro-strain values calculated from XRD data of MnO₂ and Co₃O₄/MnO₂ nanocomposites.

| Nanomaterials | δ x 10⁶ (nm⁻²) | Crystal systems | Intercept | Crystallite size (nm) | Strain(ε) |
|---------------|----------------|-----------------|-----------|----------------------|-----------|
| MnO₂          | 199.29         | Hexagonal       | -0.0969   | 2.24                 | 1.43      | 0.17038   |
| Co₃O₄/MnO₂-1-5| 28.82          | Tetragonal & Cubic | -0.02459 | 5.89                 | 5.63      | -5.05873  |
| Co₃O₄/MnO₂-1-4| 34.29          | Tetragonal & Cubic | -0.07731 | 5.4                  | 1.79      | -0.02941  |
| Co₃O₄/MnO₂-1-3| 43.40          | Complex tunnel, Tetragonal & Cubic | 0.04706  | 4.8                  | 2.94      | 0.01613   |
| Co₃O₄/MnO₂-1-2| 59.49          | Tetragonal & Cubic | -0.12931 | 4.1                  | 1.07      | -0.03866  |
| Co₃O₄/MnO₂-1-1| 81.63          | Tetragonal & Cubic | 0.18565  | 3.5                  | 0.75      | -0.08259  |

3.2. Crystallite size and strain study

3.2.1. Debye-Scherrer technique

Debye-Scherrer method (equation 1) was used to estimate the average crystallite sizes of pure MnO₂ and Co₃O₄/MnO₂ nanocomposites at different molar ratios [36, 47].

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

where, \( K \), \( D \), \( \beta \), \( \theta \) and \( \theta \) are the Scherer constant, the crystallite size, full width at the half maximum intensity, the x-ray sources wavelength and peak position, correspondingly [48]. The average value of the crystallite size of pure MnO₂, Co₃O₄/MnO₂-1-5, Co₃O₄/MnO₂-1-4, Co₃O₄/MnO₂-1-3, Co₃O₄/MnO₂-1-2, Co₃O₄/MnO₂-1-1 nanocomposites were 2.24, 5.89, 5.4, 4.8, 4.1, and 3.5 nm, correspondingly as displayed in Table 1 [49]. Moreover, the dislocation density (\( \delta \)) and strain (\( \varepsilon \)) of the electrocatalyst are additional critical factors which may be determined using the XRD data (Table 1). The \( \delta \) values for all catalysts were determined by employing equation (2).

\[
\delta = \frac{1}{D^2}
\]

where \( \delta \) and \( D \) were dislocation density and crystallite size, respectively. The result shows that \( \delta \) values increased after the addition of the dopant (Table 1).

3.2.2. Williamson-Hall technique

The crystallite size (\( D \)) and the microstrain (\( \varepsilon \)) of prepared NPs were computed via Williamson-Hall plot using Eq. (3) [6]:

\[
\beta \cos \theta = \frac{K \lambda}{D} + 4 \varepsilon \sin \theta
\]

where, \( \beta \), \( D \), \( \varepsilon \), \( K \) and \( \theta \) are the wavelength, microstrain, crystallite size, full width half maximum, and shape factor, correspondingly. A straight line was found by plotting \( \beta \cos \theta \) (y-axis) versus \( 4 \varepsilon \sin \theta \) (x-axis) and the value of the crystallite size was determined from the intercept while the value of the microstrain was determined from the slope (Figure 3) [50]. Crystallite size of 1.43 nm, 5.6 nm, 1.79 nm, 2.94 nm, 1.07 nm, and 0.75 nm were obtained for MnO₂, Co₃O₄/MnO₂-1-5, Co₃O₄/MnO₂-1-4, Co₃O₄/MnO₂-1-3, Co₃O₄/MnO₂-1-2, and Co₃O₄/MnO₂-1-1, respectively as presented in Table 1. The results show that both methods have similar crystallite sizes while showing a slight size difference. This could be because of the appearance of various particle geometries. Moreover, a -ve slope in the plot illustrates the behavior of compressive strain, whereas, the appearance of a +ve slope indicates tensile strain, which is agreed with our results [51].

3.3. ICP-OES analysis

The elemental analysis was investigated via ICP-OES to verify the amount of Co and Mn in the nanocomposites. ICP-OES samples were prepared by dissolving the as-synthesized materials in acidic solution of HNO₃:HCl, 1:3 v/v by volume. Hence, the ICP-OES analysis of the
Figure 3. Williamson Hall scheme of (a) MnO₂, (b) Co₃O₄/MnO₂-1-2, (c) Co₃O₄/MnO₂-1-4, (d) Co₃O₄/MnO₂-1-5, (e) Co₃O₄/MnO₂-1-3 and (f) Co₃O₄/MnO₂-1-1 nanocomposites.
amount of Co and Mn in the nanocomposites showed that CoO4/MnO2-1-1 sample has the higher Co and Mn content than the others, which will affect electrochemical, thermal, and structural characteristics of the nanomaterials [52]. Table 2 presents the amount of Co and Mn in the nanocomposites samples. The results showed that, the Co/Mn molar ratio in CoO4/MnO2-1-5, CoO4/MnO2-1-4, CoO4/MnO2-1-3, CoO4/MnO2-1-2 and CoO4/MnO2-1-1 samples were 0.18, 0.23, 0.29, 0.5 and 0.64, respectively, in the composite materials. The results reveal that as the amount of MnO2 increases the molar ratio of Co/Mn decreases accordingly.

3.4. BET surface area study

The surface areas of MnO2 NPs and CoO4/MnO2 nanocomposites have been examined using the BET analysis technique. Table 3 displays the BET surface area, pore volume and pore radius of as-prepared nanomaterials. The BET surface areas for the CoO4, MnO2, and CoO4/MnO2-1-1 are 80.217, 106.75 and 193.386 m2 g⁻¹, respectively. This shows that a higher surface area is conducive to the shuttle and transfer of nanomaterials [52]. Moreover, the presence of the MnO2, CoO4/MnO2-1-5, CoO4/MnO2-1-4, CoO4/MnO2-1-3, CoO4/MnO2-1-2 and CoO4/MnO2-1-1 nanocomposites were studied in 200-800 nm wavelength range of the electromagnetic spectrum (Figure 10). The absorption peaks for pure MnO2 and CoO4/MnO2 nanocomposites at various Co/Mn molar ratios were performed to identify the functional groups. The stretching and bending characteristics of various groups were analyzed in the 400 - 4000 cm⁻¹ wavelength ranges (Figure 8). As displayed in Figure 8, the band around 3411 cm⁻¹ shows the O–H stretching of H2O and the weak band at approximately at 1633 cm⁻¹ might be because of the bending vibration of O–H groups in the molecules of adsorbed water [49]. The peaks at around 1388 cm⁻¹ and 1095 cm⁻¹ are associated to O–H. However, the distinctive peaks at 592 cm⁻¹ and 520 cm⁻¹ can be matched to the stretching vibrations of M–O (M = Co, Mn). Moreover, the presence of M–O and O–H vibrations was observed from the FTIR pattern of pure MnO2 and CoO4/MnO2 [58].

Figure 9 displays the FTIR spectra of un-calcined and calcined CoO4 nanomaterials. The FTIR spectrum of CoO4 nanoparticles shows that the broad bands around 3440 cm⁻¹ is corresponding to stretching vibration of the O–H group of molecular water and the band at 1632 cm⁻¹ is matched to the bending mode of water molecules [59]. The bands at 1387 and 1074 cm⁻¹ are ascribed to the vibration of the surface bidentate carbonate from gaseous CO2 which interacts with the lattice oxygen present in CoO4 [60]. However, after annealing treatment, for the as-prepared nanoparticles at 655 cm⁻¹ is strong peak for characteristic of spinel CoO4 is noticed which is consistent to those recently reported values in the literature. The peaks around 655 and 520 cm⁻¹ are associated to vibration of the Co–O bond in CoO4 [61].

3.7. Optical property analysis

The UV-Visible absorbance spectra of pure MnO2 and CoO4/MnO2 nanocomposites were studied in 200-800 nm wavelength range of the electromagnetic spectrum (Figure 10). The absorption peaks for pure MnO2 were observed at 280 nm in the UV region while the absorption bands for CoO4/MnO2-1-5, and CoO4/MnO2-1-1 were observed at 379 and 382 nm, respectively (Figure 10(a)). The band gap values of the MnO2 and CoO4/MnO2 nanocomposites were estimated using the Tauc relationship (equation 4).

\[
(ahv)^n = A(hv - E_g)
\]

where, \(h\nu\), \(a\), \(E_g\), and \(n\) are the energy of photons, the absorption coefficient, a constant, the energy band gap, the indirect transition and the direct transition, respectively. The computed optical band gap for MnO2, CoO4/MnO2-1-5, and CoO4/MnO2-1-1 nanocomposites were 3.07 eV 2.6 eV, and 2.3 eV, correspondingly. Moreover, the band gap energy values of the as-prepared catalysts were assessed via extrapolating linear section of the sketches \((ahv)^2\) with respect to \((h\nu)\) as revealed in Figure 10 (b).

3.8. TGA/DTA study

The thermal characteristics of the CoO4, MnO2 and CoO4/MnO2 nanocomposite catalysts were studied using TGA and DTA. The analysis was performed by taking 8 mg of the synthesized materials in the range of 30-900 °C at a rate of 15 °C/min in an air atmosphere. Figure 11 displays the TGA/DTA curves of CoO4, MnO2 and CoO4/MnO2 nanocomposites. The TGA profile of the pure MnO2 NPs illustrates three steps of weight loss. In the first step 0.25 mg weight was lost before 129 °C, which can be associated with the loss of surface bonded water. In the second step 0.58
mg of weight was lost in the range of 129–556 °C, which can be attributed to the loss of lattice oxygen and phase transformation of MnO₂ to Mn₂O₃. And the third step weight loss of 0.29 mg, which may lead to additional lattice oxygen and phase transformation of Mn₂O₃ to Mn₃O₄ [62]. Similarly, the TGA profiles of the Co₃O₄/MnO₂-1-1 nanocomposites showed three steps of weight losses. The primary weight loss of 0.3 mg appeared before 164 °C showing the loss of surface adsorbed water. In the second step, the sample (0.54 mg) was lost in the range of 164–563 °C a phase transformation of MnO₂ to Mn₂O₃ and the reduction of Co₃O₄ to CoO. The third step of weight loss (0.16 mg) occurred at 563–795 °C leading to additional lattice oxygen and reduction of Mn₂O₃ to Mn₃O₄. As shown in Figure 11 the analysis was started with 8 mg of sample and then 6.88 mg and 7 mg of MnO₂ and Co₃O₄/MnO₂, respectively were obtained after heating to 900 °C, resulting in weight loss of 14% and 12.5 % of MnO₂ and Co₃O₄/MnO₂, respectively. The DTA curve for MnO₂ displays endothermic peak around 67.4 °C, which could be due to the evaporation of surface adsorbed water molecules while the large peaks at 532.7 and 609.3 °C represent the phase conversion of MnO₂ to Mn₂O₃ and from
Mn₂O₃ to Mn₃O₄, correspondingly (Figure 11 (a)). Similarly, the DTA profile of the Co₃O₄/MnO₂ nanocomposite is shown in Figure 11 (b). As exhibited in Figure 11 (b) peak around 84.8 °C was observed and this might be because of the evaporation of the bonded molecules of water. Moreover, the sharp peak was appeared at 533.5 °C and this could be owing to the phase conversion of MnO₂ to Mn₂O₃ while the peak at 589 °C might be because of a phase transformation from Mn₂O₃ to Mn₃O₄ and a reduction of Co₃O₄ to CoO [63]. Figure 11 (c) shows the thermal characteristics of Co₃O₄ nanoparticles, which proceed in three stage mass decomposition. In the first step 0.3 mg of sample was lost before 230 °C, which shows the loss of surface adsorbed water [64]. The second (0.78 mg) and third (0.4 mg) mass lost in the range of 230–437 °C and 437–698 °C were related to the decomposition of the remaining organic ligands with corresponding DTA curve at 393.2, 407.88, and 545.39 °C. However, no change is observed after 698 °C of the TGA/DTA thermal analysis patterns of Co₃O₄ nanoparticles. Thus, Co₃O₄ nanoparticles showed total weight loss of 17.5 %. Hence, the Co₃O₄, MnO₂ and Co₃O₄/MnO₂ catalysts exhibited quite different thermal characteristics because of the synergetic outcome of Co₃O₄ and MnO₂ nanomaterials. Co₃O₄/MnO₂ displayed a much stronger thermal stability with weight loss of 12.5 %.

3.9. Electrochemical characterization

3.9.1. CV study

The electrochemical ORR activities of the as-synthesized Co₃O₄, MnO₂ and Co₃O₄/MnO₂ nanocomposites modified electrodes were studied via CV under O₂ saturated atmosphere in KOH (0.1 M) aqueous medium (Figure 12) However, Figure 12 curve (c) shows the CV curve of Co₃O₄/MnO₂-1-1 modified electrode under N₂ saturated atmosphere. The oxygen reduction peaks for the as-synthesized Co₃O₄, MnO₂, Co₃O₄/MnO₂-1-1, Co₃O₄/MnO₂-1-2 and Co₃O₄/MnO₂-1-5 saturated
adsorption reactions are written as in Eqs. (8), (9), and (10) [68]:

\[ \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{HO}_{\text{ads}} + 2\text{OH}^- \] (5)

\[ 2\text{HO}_{\text{ads}} + 2e^- \rightarrow 2\text{OH}^- \] (6)

Moreover, a sharp reduction peak was not observed in the oxygen reduction peak for the as-synthesized Co$_3$O$_4$/MnO$_2$-1-1 in N$_2$ saturated atmosphere which is reliable with earlier reported results [65]. The transformation of the ORR peak toward a positive potential can be associated with a reduction in the overpotential, which enhances the ORR activity of the corresponding catalyst [66, 67]. Therefore, the reduction peak potential of the Co$_3$O$_4$/MnO$_2$-1-1 electrode was shifted by 116 mV to the positive side as compared with that of the MnO$_2$ electrode. The current intensity of Co$_3$O$_4$/MnO$_2$-1-1-modified electrode is greater that of other electrodes. The influence of saturation in oxygen in the process of catalysis was also assessed. As shown in Figure 12, the red line is the CV pattern of Co$_3$O$_4$/MnO$_2$-1-1n in the presence of oxygen and the blue line belong to the CV pattern of Co$_3$O$_4$/MnO$_2$-1-1 in the absence of oxygen. The result showed that oxygen in the cell increases the activity mechanism of Co$_3$O$_4$ and MnO$_2$ is described in Eqs. (5), (6), (7), (8), (9), (10), (11), (12), (13), (14), and (15). The two classic oxygen activity mechanism of Co$_3$O$_4$ and MnO$_2$ is described in Eqs. (5), (6), (7), (8), (9), (10), (11), (12), (13), (14), and (15) [69, 70]:

Overall: \( \text{O}_2 + \text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \) (7)

\[ \text{H}_2\text{O} + \text{O}_2 + 2e^- \rightarrow \text{HO}_{\text{ads}} + 2\text{OH}^- \] (8)

\[ \text{HO}_{\text{ads}} + e^- \rightarrow \text{HO}_2 \] (9)

Overall: \( \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2 + 4\text{OH}^- \) (10)

These two-electron reactions can be followed by further 2e$^-$ peroxide reduction or chemical peroxide disproportionation as shown below (Eqs. (11) and (12)):

\[ \text{HO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 3\text{OH}^- \] (11)

Or

\[ 2\text{HO}_2 \rightarrow 2\text{OH}^- + \text{O}_2 \] (12)

Moreover, metal oxide catalysts (i.e., Co$_3$O$_4$) follow the same ORR reaction principle on the surface with different charge distributions. However, oxygen atoms are not fully coordinated with surface cations of the stoichiometric oxide. In an aqueous electrolyte, the coordination of anions is completed through the oxygen of water molecules. Therefore, surface cations reduction via electrons from an external circuit is charge-compensated through surface oxygen ligands protonation. The reaction pathway of ORR on the surface of metal oxide is shown below (Eqs. (13), (14), and (15)) [69, 70]:

\[ \text{M}^{n+} + \text{O}^{2-} + 2e^- + 2\text{H}_2\text{O} \rightarrow 2\text{M}^{(n-1)+} + \text{OH}^- + 2\text{OH}^- \] (13)

\[ \text{O}_2 + e^- \rightarrow \text{O}_{\text{ads}} \] (14)

\[ 2\text{M}^{(n-1)+} + \text{OH}^- + \text{O}_{\text{ads}} + e^- \rightarrow 2\text{M}^{n+} + \text{O}^{2-} + 2\text{OH}^- \] (15)

### 3.9.2. LSV analysis

Further to evaluate the electrochemical properties of the as-synthesized nanoparticles, LSV tests have been performed on Co$_3$O$_4$, MnO$_2$ and Co$_3$O$_4$/MnO$_2$ nanocomposites in an oxygen-saturated KOH (0.1 M) solution at 5 mV/s scan rate (Figure 14). The Co$_3$O$_4$, MnO$_2$ and Co$_3$O$_4$/MnO$_2$ nanocomposites peaks reduced at -0.381V and -0.366V (vs Ag/AgCl), correspondingly [71]. That the cathodic current of Co$_3$O$_4$/MnO$_2$-1-1 nanocomposites modified electrode is much greater than that of Co$_3$O$_4$ and MnO$_2$ modified electrodes confirming that Co$_3$O$_4$/MnO$_2$-1-1 nanocomposite has improved electrocatalytic activity.
for oxygen reduction. The analyses display that Co$_3$O$_4$/MnO$_2$-1-1 nanocomposites have higher current and higher peak potential than Co$_3$O$_4$ and MnO$_2$ electrocatalyst.

3.9.3. Scan rate effect

CV profile of Co$_3$O$_4$/MnO$_2$ nanocomposites tests were conducted at various scan rates (5–100 mV/s) using 0.1 M KOH aqueous electrolyte saturated with oxygen by a GCE (Figure 15). Therefore, Figure 15(a) shows the voltammetric analysis of Co$_3$O$_4$/MnO$_2$-1-1 NPs at various scan rates. Scan rate studies were made to confirm the ORR performance exhibited through the Co$_3$O$_4$/MnO$_2$-1-1 NPs due to diffusion, adsorption, or a combination of them. The result shows that the cathodic peak potential at -0.297 V (5 mV/s) moved to the -ve potential as the scan rate extended to -0.365 V (100 mV/s). Furthermore, the impact of the square root of the scan rate with respect to peak current is analyzed, and a linear relationship is observed in the range of 5–100 mV/s, as presented in Figure 15(b). The result is shown as the diffusion control process, and the regression analysis is expressed in Eq. (16) [72]:

$$I_{pc} (\mu A) = 0.2292 \cdot v^{1/2} \cdot (V^{1/2} s^{-1/2}) - 1.6343, (R^2 = 0.9775)$$

Figure 10. UV-Vis profile of (a) pure MnO$_2$, Co$_3$O$_4$/MnO$_2$-1-5, and Co$_3$O$_4$/MnO$_2$-1-1, nanocomposites and Tauc plot of (b) MnO$_2$, Co$_3$O$_4$/MnO$_2$-1-5, and Co$_3$O$_4$/MnO$_2$-1-1, nanocomposites.
Figure 15(c) presents the cathodic peak current ($i_{pc}$) versus the scan rate ($v$). The presence of adsorbed electroactive species was confirmed via the linear relationship of $v$ with peak current. Hence, ORR in the Co$_3$O$_4$/MnO$_2$/GCE electrode shows kinetic control and diffusion reactions, which involves in the adsorption of O$_2$ on the electrode surface. Moreover, the relation between logarithmic sweep rate with respect to peak potential was investigated (Figure 15(d)).

The logarithm of the reduction potential with respect to the scan rate ($5$–$100$ mV/s) is presented in Eq. (17).

$$E_{pc} (V) = 0.331 \log v (V s^{-1}) + 18.37, (R^2 = 0.9165)$$  \hspace{1cm} (17)

Hence, the irreversible CV profile can be used to determine the transferred number of electrons into the reaction via Laviron method (equation 18) [73, 74]:

$$E_p = E^0 + \frac{2.303 \frac{RT}{nF}}{\alpha nF} \log \left(-\frac{RT k^0}{nF} \cdot \frac{2.303 \frac{RT}{nF}}{\alpha nF} \log v \right)$$  \hspace{1cm} (18)

where, $E^0$, $n$, $R$, $k^0$, $v$, $T$ and $\alpha$ are formal redox potential, transferred number of electrons, gas constant, standard heterogeneous rate constant of the reaction, scan rate (V s$^{-1}$), Faraday constant, temperature (K), and coefficient of transfer, correspondingly. Here, the $\alpha n$ value of 1.152 was obtained from calculated value of the slope of $E_{pc}$ vs. $\log v$ (calculated value = 0.05135), $F = 96480$ C/mol, $R = 8.314$ J/K mol and $T = 298$ K. According to Bard and Faulkner, $\alpha$ can be computed by employing Eq. (19) [75, 76];

$$\alpha = \frac{47.7}{E_p/2 - E^0}$$  \hspace{1cm} (19)

where $E_p/2$ represents the potential at half of the peak value of the current. In addition, the estimated value of $n$ to the electro-reduction process of O$_2$ on the Co$_3$O$_4$/MnO$_2$/GCE surface is 3.7. Hence, these results exhibited that the Co$_3$O$_4$/MnO$_2$ nanocomposite is a promising non-noble metal oxygen catalyst with improved catalytic performance for ORR. Table 4 shows that the assessment of electrochemical characteristics of recently investigated MnO$_2$ based electrocatalysts. Hence, the surface are the as-prepared Co$_3$O$_4$/MnO$_2$ composite (193.37 m$^2$g$^{-1}$) is lower than
those of Ag–MnO2/graphene composite (426.4 m²g⁻¹) and α-MnO2/Co₃O₄ (214.6 m²g⁻¹), however the value of n is greater than that of Ni–MnO₂ nanoneedles (n = 2.33), and approximately equivalent with Pt/C, which shows that the improvement of the electrochemical activity of the Co₃O₄/MnO₂ composite.

3.9.4. Electrochemical active surface area (ECSA) analysis

The ECSA of a catalyst is a vital performance indicator of electrochemical reaction; hence, CV of Co₃O₄, MnO₂ and Co₃O₄/MnO₂ nanocomposite synthesized catalysts are evaluated by ECSA in oxygen-saturated KOH (0.1 M) aqueous electrolyte at 50 mVs⁻¹ [82]. Figure 16 shows the reduction peak current of Co₃O₄, MnO₂, and Co₃O₄/MnO₂ nanocomposite. The peak current (Ip) increment of Co₃O₄/MnO₂ in the observed CV curve related to an irreversible two-electron transfer process using the synthesized nanomaterials as electron mediators in modified electrodes in 0.1 M KOH solution. The peak current corresponding to the reduction of Co₃O₄/MnO₂ nanocomposite increases with the interaction effect of Co₃O₄ and MnO₂. Thus, Randles-Sevcik technique (equation 20) was applied to calculate the ECSA of as-prepared electrodes [83].

\[ Ip = 268600n^{3/2}AD^{1/2}C^{1/2} \]  

where A is the ECSA of the electrode (cm²), C is the concentration of oxygen in the aqueous solution (C = 1.2 x 10⁻⁶ mol L⁻¹), Ip (A) is the peak current, D is the diffusion coefficient of oxygen in 0.1 M KOH solution (1.9 x 10⁻⁵ m² s⁻¹), n is the number of electrons transferred, and v (V/s) is the scan rate for this calculation is 50 mV/s. The ECSA values were 1.24 x 10⁻², 8.3 x 10⁻⁴, and 1.38 x 10⁻³ cm² for MnO₂, CoO₄, and Co₃O₄/MnO₂ nanocomposite modified electrodes, correspondingly (Table 5) [84]. Therefore, the larger ECSA of Co₃O₄/MnO₂/GCE results the higher double layer capacitance of Co₃O₄/MnO₂/GCE as compared to Co₃O₄ and MnO₂ electrodes.

4. Conclusions

In summary, MnO₂ and Co₃O₄/MnO₂ nanocomposites were developed by using a co-precipitation approach. The effect of molar ratio of Mn/Co in physicochemical characteristics and catalytic activity of the as-prepared materials were investigated. The electrocatalytic characteristics of as-synthesized nanomaterials were studied in 0.1 KOH alkaline media by LSV and CV test. The physicochemical and electrochemical characteristics were studied using SEM, FTIR, BET, TGA/DTA, ICP-OES and UV-Vis. The XRD result shows that a complex tunnel, hexagonal, cubic and tetragonal structure of MnO₂ NPs and MnO₂/Co₃O₄ nanocomposites with an average crystallite size of 2.24–5.89 nm. Moreover, the XRD analysis confirmed that Co₃O₄ integration with MnO₂ at different molar ratios promotes α, β, and γ-MnO₂ formation. The morphological analysis shows that MnO₂ NPs has spherical-like nanoflowers which are made of many thin nanosheets, while Co₃O₄/MnO₂ with aggregated needle-like structures. The optical band gap of MnO₂, Co₃O₄/MnO₂-1-5, and Co₃O₄/MnO₂-1-1 nanocomposites were 3.07 eV, 2.6 eV, and 2.3 eV, respectively. FTIR studies confirmed the formation of M-O spectra (M = Co, Mn) in the as-prepared NPs. The thermal examinations through TGA/DTA show that a MnO₂/Co₃O₄ nanocomposites was thermally stable associated with Co₃O₄ and MnO₂ nanoparticles. The electrochemical behaviors were analyzed via LSV and CV test for Co₃O₄, MnO₂ and MnO₂/Co₃O₄ nanocomposites. The result shows that an improved catalytic activity to ORR was obtained for the as-prepared Co₃O₄/MnO₂ nanocomposites in an alkaline condition. Thus, Co₃O₄/MnO₂ electrocatalyst with mass ratio of 1:1 showed high catalytic activity to ORR because of the synergistic effect of Co₃O₄ and MnO₂ nanoparticles. Therefore, MnO₂/Co₃O₄ nanocomposites describe highly effective, eco-friendly, durable, and cost-effective ORR electrocatalyst, which may be used in fuel cells or metal-air batteries under alkaline conditions.
Figure 15. (a) The CV patterns of GC modified Co$_3$O$_4$/MnO$_2$-1-1 electrode with several scan rates. (b) Scheme of cathodic peak current vs. $v^{1/2}$. (c) Scheme of cathodic peak current vs. $v$. (d) Scheme of $E_{pc}$ vs. log $v$.

Table 4. Comparison of recent research reports showing the ORR electrochemical properties of various MnO$_2$ based electrocatalysts.

| Active electrode material | Synthesis method | Morphology | Electrolyte | Surface area (m$^2$ g$^{-1}$) | Electrochemical property | $n$ | Ref. |
|--------------------------|-----------------|------------|-------------|-----------------------------|-------------------------|-----|------|
| Co$_3$O$_4$/MnO$_2$ composite | Co-precipitation | Needle-like structure | 0.1 M KOH | 193.37 | Shows the ORR potential (V) at -0.352 V (vs. Ag/AgCl) | 3.7 | This work |
| Ag-MnO$_2$/graphene composite | Immersion-calcination | Nanoparticles | 0.1 M KOH | 426.4 | Onset potential of 0.068 V and ORR reaction limiting current density of 5.62 mA cm$^{-2}$ | 3.9 | [77] |
| $\alpha$-MnO$_2$ and Co$_3$O$_4$ | One-step solution-based | Microspheres & nanoparticulate | 0.1 M KOH | 214.6 | Half-wave potential and potential of -0.197 and -0.226 V (vs. Ag/AgCl) at -3 mA cm$^{-2}$ | 3.94 | [78] |
| Pt/C | - | Amorphous | 0.1 M KOH | - | Shows current density of 5.02 J/mA cm$^{-2}$ | 3.89 | [79] |
| PVP- MnO$_2$/CNT | Hydrothermal | Aggregates | 0.1 M of aqueous Na$_2$SO$_4$ | - | Shows the ORR potential (V) at -0.43 (vs. Ag/AgCl) | - | [80] |
| MnO$_2$/rGO | Electrodeposition | Yarn-rod shape | 0.1 M KOH | 50.5 | Shows the ORR potential (V) at -0.36 V | 3.92 | [79] |
| Ni–MnO$_2$ nanoneedles | Hydrothermal | Nanoneedle | 0.1 M KOH | - | Shows the current densities of -1.24 mA cm$^{-2}$ with a reduction potentials of -0.43 V | 2.33 | [81] |
Table 5. ECSA values for different catalysts computed via Randles-Sevick equation.

| No. | Catalyst | ECS Area (cm²) |
|-----|----------|----------------|
| 1   | Co₃O₄ NPs | 8.3 x 10⁻⁴ |
| 2   | MnO₂ NPs  | 1.24 x 10⁻³ |
| 3   | Co₃O₄/MnO₂-1-1 | 1.38 x 10⁻³ |

Declarations

Author contribution statement

Ababay Ketema Worku: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Delele Worku Ayele, Nigus Gabbiye Habtu: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Temesgen Atnafu Yemata: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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