Influence of nickel doping on MnO₂ nanoflowers as electrocatalyst for oxygen reduction reaction

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Abstract

Doping is promising strategy for the alteration of nanomaterials to enhance their optical, electrical, and catalytic activities. The development of electrocatalysts for oxygen reduction reactions (ORR) with excellent activity, low cost and durability is essential for the large-scale utilization of energy storage devices such as batteries. In this study, MnO₂ and Ni-doped MnO₂ nanowires were prepared through a simple co-perception technique. The influence of nickel concentration on electrochemical performance was studied using linear sweep voltammetry and cyclic voltammetry. The morphological, thermal, structural, and optical properties of MnO₂ and Ni-doped MnO₂ nanowires were examined by SEM, ICP-OES, FT-IR, XRD, UV–Vis, BET and TGA/DTA. Morphological analyses showed that pure MnO₂ and Ni-doped MnO₂ had flower-like and nanowire structures, respectively. The XRD study confirmed the phase transformation from ϵ to α and β phases of MnO₂ due to the dopant. It was also noted from the XRD studies that the crystallite sizes of pure MnO₂ and Ni-doped MnO₂ were in the range of 2.25–6.6 nm. The band gaps of MnO₂ and 0.125 M Ni-doped MnO₂ nanoparticles were estimated to be 2.78 and 1.74 eV, correspondingly, which can be seen from UV–Vis. FTIR spectroscopy was used to determine the presence of functional groups and M–O bonds (M = Mn, Ni). The TGA/TDA examination showed that Ni-doping in MnO₂ led to an improvement in its thermal properties. The cyclic voltammetry results exhibited that Ni-doped MnO₂ nanowires have remarkable catalytic performance for ORR in 0.1 M KOH alkaline conditions. This work contributes to the facile preparation of highly active and durable catalysts with improved catalytic performance mainly due to the predominance of nickel.

Article Highlights

- MnO₂ and Ni-doped MnO₂ nanowires were synthesized via a facile co-perception approach.
- Nickel doping in MnO₂ induces the formation of wire-like nanostructures.
- Nickel doping enhances the electrochemical activity and thermal stability of MnO₂ nanoflowers.
- The addition of nickel into MnO₂ promoted the catalytic activity for oxygen reduction reaction.
- A higher catalytic activity was achieved in 0.125 M Ni-MnO₂ nanowires.

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Graphic abstract

Keywords Oxygen reduction reaction · Co-precipitation method · MnO₂ nanoflowers · Ni-doped MnO₂ nanowires

1 Introduction

Globally, the focus on low-carbon emissions and the concept of sustainability has notably proposed the development of sustainable energy sources [1, 2]. Electrochemical energy storage tools such as metal-air batteries (MABs) and fuel cells are considered to play a significant impact in the transformation to a sustainable prospect [3–5]. Moreover, one of the main problems that restrict the application of lithium-ion batteries for electric vehicles is its low specific energy density [6, 7]. Recently, special attention is given to the performance enhancement of MABs due to their extraordinary ideal energy density and low cost, mainly in lithium-air and zinc-air batteries (ZABs) [8–10]. Hence, ZABs have a low cost, comparatively higher energy density, and excellent safety [11, 12]. However, the fabrication with effective air electrodes is found to be the critical problem associated with ZABs [13, 14]. The challenges of air electrodes can be solved by preparing active, efficient, stable and durable oxygen catalysts for the ORR [15]. The ORR is a vital cathodic reaction in fuel cells and MABs [16, 17]. Precious metals such as Platinum (Pt) and Pt-based alloys are the most effective ORR electrode substances [18, 19]. However, the application of Pt and its derivatives as ORR catalysts is limited because of their poor stability, limited access, and high price [20,

21]. Hence, to address these concerns, strategies have been designed to prepare highly-active, durable, and more stable non-precious metal-based ORR catalysts [22, 23]. Transition metals, metal oxides, and carbon-based materials can be used as alternative electrocatalysts [24, 25]. Among transition metal oxides, MnO₂ can be used as an air electrocatalyst for the ORR due to its excellent catalytic performance, abundance, low price, and environmental safety [26–28]. Moreover, MnO₂ is particularly promising material because of its mild preparation, stable thermal behavior, and excellent overall performance [29, 30]. However, the performance of MnO₂ is restricted by its inherently poor electronic conductivity, low structural stability, and ion conductivity [31, 32]. Hence, the emerging approach to increase the electronic conductivity and electrochemical performance of MnO₂ nanoparticles (NPs) is to combine with high conductive substances such as graphene, carbon nanotubes, and carbon fibers [33, 34]. An alternative approach is defect engineering, in which foreign elements should be doped to improve the inherent electronic conductivity and enhance the concentration of redox-active sites [35, 36]. The incorporation of different foreign element into MnO₂ NPs, particularly defect engineering, has been considered as an effective technique to enhance its electronic conductivity [37]. For enhanced ORR catalyst activity, different metals have been doped

into MnO_2 such as Iron (Fe), Nickel (Ni) [38], Chromium (Cr), Cobalt (Co) [39], Copper (Cu) [40], Molybdenum (Mo) [41], Aluminum (Al) [42], and Vanadium (V) [43]. Those results exhibited that doping improves the overall performance of MnO_2 NPs [44]. One on hand different approaches have been investigated for the synthesis of MnO_2 NPs such as emulsion, sol-gel, co-precipitation, thermal decomposition [45], simple reduction, and hydrothermal approach [46, 47]. However, those approaches are expensive, needs sophisticated instruments, and relatively longer preparation time [48, 49]. Among these, the co-precipitation approach is advantageous due to easy, fast, cost-effective, and easy to control during preparation [50, 51]. Many studies have been investigated on optical, electrical, and magnetic characteristics of Ni doped MnO_2 nanoparticles [52]. However, only a few studies have been reported about the structural, morphological, thermal, and electrochemical characteristics of Ni-doped MnO_2 NPs by defect engineering at ambient conditions. Herein, we examined the influence of nickel doping on structural, morphological, thermal, and electrochemical characteristics of MnO_2 NPs prepared by a facile co-precipitation approach [53, 54].

2 Materials and methods

2.1 Materials

All chemicals and reagents were used without any refinement and of analytical grade. Ethanol, Vulcan XC 72 carbon

powder, and isopropanol were obtained from India (Alpha Chemika). Potassium permanganate (KMnO_4 , 99.5%), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%) and manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 99%) were obtained from Fluka (Germany). The solutions were prepared by using distilled water.

2.2 Synthesis of Ni-doped MnO_2 NPs

Nickel doped- MnO_2 nanowires were developed using a facile co-precipitation technique. In a typical synthesis, 0.3 M of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and the preferred mole of (0.025, 0.05, 0.75, 0.1, and 0.125 M) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 mL distilled water. Then, 0.2 M potassium permanganate solution dissolved in 100 mL of distilled water was added drop wise to the combination of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. The mixture was stirred at 300 rpm at 60 °C for 5 h. The pH of the mixture was adjusted to 12 by adding 0.2 M NaOH solution. Then, the product was filtered and washed with distilled water and ethanol. Moreover, the as-prepared samples were dried at 80 °C for 8 h to evaporate water and organic materials. Finally, the products were annealed in a muffle furnace at 500 °C for 4 h. A similar technique was used to prepare pure MnO_2 . The detailed schematic illustration of Ni-doped MnO_2 nanowires prepared by the co-precipitation route is shown in Fig. 1.

Fig. 1 The synthesis route of Ni-doped MnO_2 nanowires prepared via co-precipitation technique

2.3 Characterization

The functional groups were studied using Fourier transform infrared spectrometer (FT-IR, FT-IR 6660 (JASCO MODEL)) in the wavenumber range of 4000–400 cm^{-1} , in a standard KBr pellet method. The crystal structures of the synthesized nanoparticles were examined using X-ray diffraction (MAXima_X XRD-7000, SHIMADZU) using radiation of $\text{Cu-K}\alpha$. XRD analysis at room temperature in 2θ range between 10° and 80° . It was continuously scanned at a step size of 0.02° with a counting time of 0.30 s per step with a scan speed of 4.0 (deg/min) operating at 30 mA and 40 kV with a divergence slit of: 1.0° , scatter slit: 1.0° , receiving slit: 0.30 (mm). Scanning electron microscopy (SEM, INSPECT F50) was used to examine the morphological properties of as-prepared NPs. A thermal property study was performed using the TGA/DTA study. Ultraviolet–visible spectrophotometer (UV–Vis, Lambda 35 (PerkinElmer)) in the wavelength range of 200–800 nm was conducted to analyze the optical characteristics of prepared NPs. Brunauer–Emmett–Teller (BET, Quanta chrome Instruments version 11.0) was used to determine the specific surface areas of as-prepared nanoparticles. After dissolving the synthesized materials in HCl and HNO_3 aqueous solution, the composition of Ni and Mn in the Ni-MnO_2 product was analyzed via inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer 800). Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were done for electrochemical analysis using CHI760E electrochemical workstation.

2.4 Preparation of working electrode

To examine the electrochemical characteristics of the developed MnO_2 and Ni-doped MnO_2 NPs, the working electrode was fabricated as follows: MnO_2 and Ni-doped MnO_2 nanoparticle samples were combined with carbon powder at a mass ratio of 30:70 to ensure adequate electronic conductivity. Then, 5 mg of MnO_2 and Ni-doped MnO_2 catalysts (dispersed in 1 mL mixed solution of water/isopropanol, 2.5:1 v/v) was sonicated for 30 min to form a uniform ink. Then 5 μL of the catalyst solution was pipetted onto a glassy carbon electrode (GCE) of 3 mm diameter and dried at room temperature.

2.5 Electrochemical characterization

Electrochemical analyses were accomplished using a computer-controlled potentiostat (CHI760E electrochemical workstation) equipped with a three-electrode conventional cell. The electrocatalytic characteristics were analyzed by LSV and CV. CV was estimated in a 0.1 M KOH electrolyte using platinum coil and Ag/AgCl as a counter

Fig. 2 XRD patterns of (a) MnO_2 , (b) Ni-MnO_2 (0.025 M), (c) Ni-MnO_2 (0.05 M), (d) Ni-MnO_2 (0.075 M), (e) Ni-MnO_2 (0.1 M), (f) Ni-MnO_2 (0.125 M) NPs

and reference electrode, respectively. All potentials stated in this study were referenced to the Ag/AgCl electrode. For CV analyses, the working electrode was examined between +0.1 to -0.7 V at a sweep rate of 5, 10, 20, 50, and 100 mV s^{-1} at room temperature via saturating the electrolyte through O_2 for 30 min. LSV analysis was done at a scan rate of 5 mV s^{-1} in +0.1 to -0.7 V (vs. Ag/AgCl) of potential range.

3 Results and discussion

3.1 Structure analysis

The crystalline size, structure, and phase purity, of the MnO_2 and Ni-MnO_2 samples were examined using XRD. The XRD patterns of the MnO_2 and Ni-MnO_2 nanoparticles are shown in Fig. 2. Figure 2a shows the diffraction peaks of MnO_2 at 2θ angles of 37.03° , 42.65° , 56.44° , and 66.11° are attributed to the diffraction of (1 0 0), (1 0 1), (1 0 2), and (1 1 0) crystal planes of akhtenskite $\epsilon\text{-MnO}_2$ (JCPDS 00–030–0820). In contrast, the Ni-doped MnO_2 sample in Fig. 2b, c shows sharp diffraction peaks at 28.55° , 37.03° , 42.75° , 56.44° , and 72.58° , which can be indexed to the (110), (101), (111), (211), and (112) crystal planes of $\beta\text{-MnO}_2$ (JCPDS card 00–024–0735) and the peaks at 2θ values of 37.13° , 62.46° , and 76.44° , were corresponding to the (111), (220), and (311) planes of NiO (JCPDS card no: 00–047–1049), respectively. The XRD pattern with a sharp peak indicates the excellent crystallinity of the prepared

sample. The sharp diffraction peaks at 2θ of 12.72° , 17.93° , 28.65° , 37.03° , 42.44° , 49.70° , 56.65° , 60.11° , 65.84° , 69.10° , and 72.98° , match to the (110), (200), (310), (211), (301), (411), (600), (521), (002), (541), and (312) are the crystal planes of α - MnO_2 (JCPDS card NO. 00-044-0141) [55]. Whereas the diffraction peaks shown in Fig. 2e–f at 2θ angles of 37.03° , 42.65° , 56.44° , and 66.11° correspond to the (1 0 0), (1 0 1), (1 0 2), and (1 1 0) crystal planes of akhtenskite ϵ - MnO_2 (JCPDS 00–030–0820) and the peaks at 2θ values of 37.13° , 62.46° , and 76.44° are correspond to the (111), (220), and (311) crystal planes of NiO (JCPDS card no: 00–047–1049). It was also noted that nickel contents has an effect on crystal structure of MnO_2 . The slight change in the peak intensity of nickel-doped MnO_2 samples are due to the size change of the nanoparticles. Thus, nickel doping promotes the formation of α , and β - MnO_2 nanoparticles [56].

3.2 Crystallite size analysis

3.2.1 Scherrer technique

The average crystallite sizes of pure MnO_2 and Ni- MnO_2 NPs at different doping level were determined by using the Scherrer Eq. (1) [57].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where λ , K , D , θ , and β are wavelength of the x-ray sources, Scherrer constant, crystallites size, peak position and full width at the half maximum intensity (FWHM), respectively [2]. The estimated crystallite size of MnO_2 , Ni- MnO_2 (0.025 M), Ni- MnO_2 (0.05 M), Ni- MnO_2 (0.075 M), Ni- MnO_2 (0.1 M), and Ni- MnO_2 (0.125 M) NPs were 2.25, 4.03, 5.3, 6.6, 5.52, and 6.1 nm, correspondingly (Table 1). The dislocation density and strain of the MnO_2 and Ni- MnO_2 NPs are other vital determinants that can be calculated from the XRD analysis. The dislocation density (δ) values were estimated using Eq. (2).

$$\delta = 1/D^2 \quad (2)$$

where D and δ are crystallites size and dislocation density, respectively. Hence, the addition of dopant increases the dislocation density of the NPs.

3.2.2 Williamson–Hall method

A Williamson–Hall plot was drawn to determine the lattice strain and effective crystallite size using Eq. (3) [7]:

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\epsilon \sin \theta \quad (3)$$

where K , β , D , λ and ϵ are shape factor, full width hall maximum, crystallite size, wavelength, and microstrain, respectively. Therefore, the graph was plotted within “ $4\sin\theta$ ” on x-axes and “ $\beta\cos\theta$ ” on the y-axis, and a straight line was obtained. The intercept of a straight line is the crystallite size whereas slope provides the value of the microstrain as presented in Fig. 3. The crystallite size of MnO_2 , Ni- MnO_2 (0.025 M), Ni- MnO_2 (0.05 M), Ni- MnO_2 (0.075 M), Ni- MnO_2 (0.1 M), and Ni- MnO_2 (0.125 M) NPs were 1.43, 1.73, 3.24, 3.77, 1.39, and 4.92 nm, correspondingly (Table 1). It was noticed that both methods gave very close crystallite size.

3.3 Morphology analysis

The morphologies of MnO_2 and Ni-doped MnO_2 were studied using SEM. Figure 4 displays the SEM image of MnO_2 NPs, which have a flower-like structure and a diameter of 4.7 nm. This flower-like structure is composed of different self-assembled irregular nanosheets. On the other hand, 0.025 M Ni-doped MnO_2 has agglomerated small nanoneedles of porous morphology with an average particle size of 7.13 nm (Fig. 5). This suggested that, the addition of nickel affected the surface morphology of MnO_2 , as shown in Fig. 5. Moreover, 0.125 M Ni-doped MnO_2 consisted of nanowires with an average particle size of 7.07 nm, which implies the key role of Ni^{+2} is regulating the nanostructures of MnO_2 (Fig. 6). The average diameter of as-prepared nanowires were analysed via particle size distribution histogram computed from SEM image via Image J software as shown in Fig. 7a–c. Generally, when Ni^{2+} were

Table 1 Computed microstrain and crystallite parameters from XRD data study of MnO_2 and Ni-doped MnO_2 NPs

Nanomaterials	Crystal systems	$\delta \times 10^3 \text{ (nm}^{-2}\text{)}$	Crystallite Size (nm)		Strain(ϵ) from W–H plot
			Scherrer	W–H	
MnO_2	Hexagonal	197.53	2.25	1.43	0.17004
0.025 M Ni- MnO_2	Tetragonal	61.57	4.03	1.73	–0.01198
0.05 M Ni- MnO_2	Tetragonal	35.59	5.3	3.24	–0.00365
0.075 M Ni- MnO_2	Tetragonal	22.95	6.6	3.77	–0.01081
0.1 M Ni- MnO_2	Hexagonal	32.81	5.52	1.39	–0.03127
0.125 M Ni- MnO_2	Hexagonal	26.87	6.1	4.92	–0.00354

Fig. 3 Williamson Hall plots of (a) pure MnO_2 , (b) 0.025 M Ni-MnO_2 , (c) 0.05 M Ni-MnO_2 , (d) 0.075 M Ni-MnO_2 , (e) 0.1 M Ni-MnO_2 , and (f) 0.125 M Ni-MnO_2 NPs

Fig. 4 SEM images of a pure MnO_2 NPs at 400 nm, b pure MnO_2 NPs at 5 μm , c pure MnO_2 NPs at 10 μm

added the original flower-like structures started to dissolve and slowly change into the shape of the sphere and finally nanowires. It can be noted from the SEM images that there is an obvious distinction in morphologies between pure and Ni-doped MnO_2 nanomaterials indicating that the

doping level of Ni cations has a vital effect on the morphologies of MnO_2 NPs. Thus, Ni-doped MnO_2 NPs show high porosity and better particle dispersion than that of MnO_2 NPs, which is a promising property to enhance the catalytic performance of the as-prepared NPs.

Fig. 5 SEM images of **a** 0.0125 M Ni-doped MnO_2 NPs at 500 nm, **b** 0.0125 M Ni-doped MnO_2 NPs at 3 μm , and **c** 0.0125 M Ni-doped MnO_2 NPs at 10 μm

Fig. 6 SEM images of **a** Ni-doped MnO_2 (0.125 M) NPs at 500 nm, **b** Ni-doped MnO_2 (0.125 M) NPs at 1 μm , and **c** Ni-doped MnO_2 (0.125 M) NPs at 3 μm

Fig. 7 Histogram scheme showing a particle size distribution of **a** MnO_2 , **b** 0.025 M Ni-doped MnO_2 and **c** 0.125 M Ni-doped MnO_2 NPs

3.4 ICP-OES analysis

Elemental compositions studies of the as-prepared samples were examined by ICP-OES to confirm the amount of Mn and Ni loaded in Ni-doped MnO_2 nanoparticles. ICP-OES analysis were conducted via dissolving the

as-prepared nanoparticle in a concentrated acidic solution ($\text{HCl}:\text{HNO}_3$, 3:1 v/v by volume). Table 2 displays the content of Ni and Mn in the Ni-doped MnO_2 nanoparticles. Moreover, the Ni/Mn doped molar ratio in Ni-doped MnO_2 nanoparticles were 0.025, 0.066, 0.086, 0.137 and 0.103 for Ni-MnO₂ (0.025 M), Ni-MnO₂ (0.05 M), Ni-MnO₂ (0.075 M),

Table 2 Ni-doped MnO₂ nanoparticles analysis results through ICP-OES

Nanomaterials	Ni (mmol/L)	Mn (mmol/L)	Ni/Mn
Ni-MnO ₂ (0.025 M)	0.013	0.514	0.025
Ni-MnO ₂ (0.05 M)	0.027	0.408	0.066
Ni-MnO ₂ (0.075 M)	0.033	0.382	0.086
Ni-MnO ₂ (0.1 M)	0.056	0.409	0.137
Ni-MnO ₂ (0.125 M)	0.044	0.428	0.103

Table 3 BET specific surface area, pore-volume, and pore radius of MnO₂ and Ni-MnO₂ NPs

Samples	Surface area (m ² /g)	Pore volume (cc/g)	Pore radius (Å)
MnO ₂	95.619	0.297	34.056
0.1 M Ni-MnO ₂	103.475	0.325	34.92
0.125 M Ni-MnO ₂	124.386	0.506	34.257

Ni-MnO₂ (0.1 M), and Ni-MnO₂ (0.125 M) nanoparticles, respectively. Hence, the ICP-OES analysis results showed that 0.1 M Ni-MnO₂ and 0.125 M Ni-MnO₂ nanoparticles have the higher Ni/Mn molar ratio than the others, which affects the thermal, structural, and electrochemical properties of the nanoparticles [58].

3.5 Surface area analysis

BET analysis techniques have been utilized to determine the textural properties such as specific surface areas, pore volume and pore size of MnO₂ and Ni-MnO₂ nanoparticles. Table 3 presents the BET surface area, pore radius and pore volume of MnO₂, Ni-MnO₂ (0.1 M), and Ni-MnO₂ (0.125 M) NPs. The BET analysis display a specific surface area of 95.619, 103.475, and 124.386 m² g⁻¹ for MnO₂, Ni-MnO₂ (0.1 M) and Ni-MnO₂ (0.125 M) NPs, respectively. The corresponding pore radius was 34.056, 34.92, and 34.257 Å for MnO₂, 0.1 M Ni-MnO₂, and 0.125 M Ni-MnO₂ NPs, respectively. Hence, 0.125 M Ni-MnO₂ nanoparticles exhibited the largest BET surface area, which is ascribed to porous structure. The porous structure enables the transfer and diffusion of electrolyte ions through the charging and/or discharging process. Thus, the doping of nickel in MnO₂ nanoparticles leads to an increment of the BET surface area [59].

3.6 FT-IR analysis

FT-IR spectroscopy was accomplished within 400 to 4000 cm⁻¹ ranges of the electromagnetic spectrum. Figure 8 illustrates the typical FT-IR spectra of MnO₂ and Ni doped MnO₂ NPs at various doping level. As shown in Fig. 8, the band approximately at 3433 cm⁻¹ shows O–H stretching in water molecules, and the small band nearly

Fig. 8 FTIR spectra of MnO₂, Ni-MnO₂ (0.025 M), Ni-MnO₂ (0.05 M), Ni-MnO₂ (0.075 M), Ni-MnO₂ (0.1 M), and Ni-MnO₂ (0.125 M) NPs

Fig. 9 UV-Vis spectra of **a** pure MnO_2 and Ni-MnO_2 NPs, and **b** Tauc scheme of pure MnO_2 and Ni-MnO_2 NPs

at 1633 cm^{-1} may be because of bending vibration of O–H groups in the adsorbed water molecules. Moreover, the bands approximately at 1386 and 1092 cm^{-1} match to the coordination of Mn by the O–H. Finally, the characteristic peak at 578 cm^{-1} , and 518 cm^{-1} can be associated with the stretching vibrations of M–O or M–O–M (M = Ni, Mn). Hence, the appearance of M–O or M–O–M bond and O–H was confirmed from the FTIR band of MnO_2 and Ni-MnO_2 NPs. The FT-IR spectra observed in this study are consistent with previously reported results [59].

3.7 UV-visible analysis

To study optical characteristics of the as-prepared samples, UV-Vis analysis were performed between 200 and 800 nm. Figure 9a illustrates UV-visible spectrum of MnO_2 and Ni-doped MnO_2 NPs. It was observed that MnO_2 showed absorption peaks at 318 nm [40]. Furthermore, the characteristics absorption bands at 378 nm corresponded to Ni-doped MnO_2 nanoparticles sample. The optical band gap of MnO_2 and Ni-doped MnO_2 sample were computed using Tauc relationship (Eq. 1) [60].

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (4)$$

where α , $h\nu$, and A are the absorption coefficient, photon energy and constant. Figure 9b shows the energy band gap values of MnO_2 and Ni-MnO_2 NPs computed by extrapolating the linear part of these plots of $(\alpha h\nu)^2$ axis to $(h\nu)$ axis. The results showed that 2.78 and 1.74 eV were band gap energy of MnO_2 and Ni-doped MnO_2 NPs, respectively. UV-Vis investigation showed that Ni-doped MnO_2 NPs with enhanced electronic conductivity.

3.8 Thermal analysis

TGA and DTA analysis were investigated to study the thermal and phase evolution properties of pure MnO_2 and Ni-MnO_2 NPs. The as-prepared NPs were heated in the range of $25\text{--}950\text{ }^\circ\text{C}$ with $10\text{ }^\circ\text{C min}^{-1}$ heating rate in air atmosphere. Figure 10 presents the TGA/DTA curve of pure MnO_2 and Ni-MnO_2 NPs. In the TGA curve of pure MnO_2 , the first (0.47 mg) weight loss occurs between 25 and $278\text{ }^\circ\text{C}$, and the corresponding endothermic peak observed at $70\text{ }^\circ\text{C}$ may be because of the loss of adsorbed water. The next weight loss of 0.43 mg in the range of $278\text{--}564\text{ }^\circ\text{C}$ can be due to the phase change of MnO_2 to Mn_2O_3 . Thus, the weight loss of 0.19 mg in between 564 and $838\text{ }^\circ\text{C}$ can be associated with the phase change of Mn_2O_3 to Mn_3O_4 . Moreover, in the DTA curve of pure MnO_2 the two sharp exothermic and endothermic peaks that arise at $588\text{ }^\circ\text{C}$ and $815\text{ }^\circ\text{C}$, respectively that might be due to a variation in crystallinity or possibly due to a phase transition in the NPs. A final weight of 6.91 mg was obtained from the initial weight of 8 mg which corresponds to 13.6% weight loss when heated to $950\text{ }^\circ\text{C}$ (Fig. 10a). Similarly, the 0.125 M Ni-MnO_2 TGA curve, shows the first weight loss of 0.55 mg approximately at $385\text{ }^\circ\text{C}$, and the corresponding endothermic peak at $117\text{ }^\circ\text{C}$ may be due to loss of physically adsorbed water (Fig. 10b). The next weight loss of 0.17 mg in the range of $385\text{--}569\text{ }^\circ\text{C}$ could be due to the phase change of MnO_2 to Mn_2O_3 . Finally, the weight loss of 0.27 mg in between 569 and $882\text{ }^\circ\text{C}$ can be associated with the phase change of Mn_2O_3 to Mn_3O_4 . Moreover, in the DTA curve of pure MnO_2 , the two sharp exothermic and endothermic peaks that arise at $586\text{ }^\circ\text{C}$ and $874\text{ }^\circ\text{C}$,

Fig. 10 TGA/DTA illustration of **a** MnO₂ NPs, and **b** Ni-doped MnO₂ (0.125 M) NPs

respectively, which might be due to a variation in crystallinity or possibly due to a phase transition in the NPs. Hence, we observe that the study was begun with 8 mg of catalyst, and after complete heating up to 950 °C, the catalyst remained was 7.01 mg. Thus, the percentage weight loss for our analysis up to 950 °C, is 12.36%. Generally, in our analysis weight loss of 13.63% and 12.36% is associated to MnO₂ and Ni-MnO₂ NPs, correspondingly. Hence, our analysis showed that Ni-MnO₂ NPs with improved thermally stability. The TGA and DTA result showed similarities with the previously reported results. However, slight

change in the peak positions were observed at different stages, which may be due to the use of different reagents in the synthesis process [61].

3.9 Electrochemical studies

3.9.1 CV study

The catalytic activity of un-doped MnO₂ and Ni-MnO₂ electrocatalysts were analyzed using CV in O₂-saturated KOH (0.1 M) solution (Fig. 11). Figure 11a which exhibits

Fig. 11 CV curve of; **a** pure MnO_2 and Ni doped MnO_2 nanoparticles at 50 mV/s scan rate, **b** 0.125 M Ni doped MnO_2 at different scan rates, and **c** MnO_2 at different scan rates

the (CV) curves of pure MnO_2 , 0.1 M Ni-MnO_2 , and 0.125 M Ni-MnO_2 in a 0.1 M KOH solution. For pure MnO_2 electrode, the reduction peak was present at -0.361 V (vs. Ag/AgCl). The ORR peak potential of 0.1 M Ni-MnO_2 , and 0.125 M Ni-MnO_2 is placed at -0.348 V, and -0.348 V (vs. Ag/AgCl), correspondingly. The result showed that the 0.1 M Ni-MnO_2 and 0.125 M Ni-MnO_2 reduction potential were shifted by 13 mV to the positive direction compared to pure MnO_2 . Moreover, at the potential of -0.348 V (vs. Ag/AgCl), the current of the ORR at the electrode with a catalyst 0.125 M Ni-MnO_2 is $38.56 \mu\text{A}$, which is higher than that of the electrode with pure MnO_2 ($32.17 \mu\text{A}$). The ORR peak current of Ni-MnO_2 catalyst is bigger than that

of pure MnO_2 catalyst [24]. The findings are in agreement with previously reported results [44, 62]. It can be said that the as-prepared MnO_2 and Ni-doped MnO_2 electrocatalysts are to be an ideal air electrode material for metal-air batteries and fuel cells. Figure 11b, c illustrates the CV illustration of un-doped MnO_2 and Ni-MnO_2 nanowires at numerous scan rates. The effect of scan rate in between 5 and 100 mV/s was studied at pure MnO_2 and 0.125 M Ni-MnO_2 modified electrode. Figure 11b, c shows the largest variation between the four ORR curves where a negative peak potential shifts with increase of scan rate are observed, which is detected when the oxidation reaction is irreversible. Hence, the ORR activities of MnO_2 and

Fig. 12 CV curve of saturated and unsaturated MnO_2 and 0.125 M Ni-doped MnO_2 NPs at 50 mV/s scan rate

Fig. 13 LSV sketch of un-doped MnO_2 and Ni- MnO_2 (0.125 M) NPs at 5 mVs⁻¹ scan rates

Ni- MnO_2 catalysts are also dependent on the scan rates. The result showed that excellent ORR catalytic activity can be obtained at lower scan rate [63, 64]. Figure 12 shows the ORR activity of pure MnO_2 , and 0.125 M Ni- MnO_2 modified electrode before saturation and after oxygen saturation. The result showed that un-saturated pure MnO_2 with better catalytic performance but poor current intensity. Moreover, un-saturated 0.125 M Ni- MnO_2 modified electrode showed poor catalytic performance and current intensity. It is notably seen that nickel doped (0.1 M Ni- MnO_2 and 0.125 M Ni- MnO_2) electrode displayed excellent reduction peak potential, which confirms a higher electrocatalytic activity to ORR due to the synergistic effect of nickel and MnO_2 .

3.9.2 LSV analysis

ORR activity of the un-doped MnO_2 and Ni- MnO_2 (0.125 M) NPs were evaluated using linear scanning voltammetry (LSV). Figure 13 shows the LSV profile of MnO_2 and Ni doped MnO_2 (0.125 M) nanoparticles in O_2 -saturated KOH (0.1 M) alkaline media at a scan rate of 5 mV s⁻¹ from +0.1 to -0.7 V (vs. Ag/AgCl). As it can be seen in Fig. 13, the reduction peak potential of MnO_2 and 0.125 M Ni doped MnO_2 nanoparticles appear at -0.389 V and -0.372 V (vs. Ag/AgCl), respectively. Thus, 0.125 M Ni- MnO_2 NPs shows relatively better ORR catalytic performance compared to that of un-doped MnO_2 with more positive current and peak potential. Hence, more content of Mn^{3+} in MnO_2 and large surface area leads to better electro-catalytic performance of Ni doped MnO_2 [65].

3.9.3 CV scans rate analysis

CV analyses were conducted by changing the scan rate between 5 and 100 mV/s (Fig. 14a). Scan rate analysis can reveal whether the electrocatalytic activity of Ni-doped MnO_2 NPs on ORR is controlled by diffusion, adsorption and even these two processes. The plot of cathode peak current (i_{pc}) with the scan rate (v)^{1/2} and the square root of the scan rate (v) are shown in Fig. 14b, c. It is observed that a linear relationship between the cathode peak current versus $v^{1/2}$ and v values (Fig. 14b, c). The linear relationship of peak current and $v^{1/2}$ shows a diffusion control process. Moreover, the peak current is also linearly related to v , which means that there is adsorbed electroactive species. These result show that the ORR on the Ni- MnO_2 /GCE is a combination of kinetic and diffusion control reactions, involving the adsorption of O_2 on the surface of the electrode [66]. The involved numbers of electrons (n) in the catalytic reaction of irreversible CV behaviour have been calculated via Laviron equation. The linear relationship among logarithmic sweep rate and peak potential is shown in Fig. 14d. The logarithm of the reduction potential and the scan rate is in the range of 5–100 mV/s as shown in Eq. (5).

$$E_{pc}(V) = 0.3315 \log v(Vs^{-1}) + 18.3704, \quad (R^2 = 0.9165) \quad (5)$$

In addition, Laviron equation of irreversible CV characteristics is utilized to estimate the transferred number of electrons (n) in the electrocatalytic reaction as shown in Eq. (6) [67]:

$$E_p = E^{0'} + \left(\frac{2.303RT}{\alpha nF} \right) \log \left(\frac{RTk^0}{\alpha nF} \right) + \left(\frac{2.303RT}{\alpha nF} \right) \log v \quad (6)$$

where k^0 , $E^{0'}$, v , n , α , F , R and T are standard heterogeneous rate constant of the reaction, formal redox potential, scan

Table 4 Comparison of electrochemical properties of recently studied MnO₂ based electrocatalysts for ORR

Active electrode material	Synthesis method	Morphology	Electrolyte	Surface area (m ² g ⁻¹)	Electrochemical property	n	References
Ni- α -MnO ₂	Hydrothermal	Nanowires	0.1 M KOH	52.3	Shows onset potentials at 0.88–0.89 V	3.6	[65]
Cu- α -MnO ₂ Nanowire	Hydrothermal reaction	Nanowires	0.1 M KOH	83.8	At 10 mV shows (–0.097 V and –0.100 V vs. Ag/AgCl)	3.2–3.3	[69]
Transition metal ions-doped MnO ₂	Carbonization	Nanosheets	0.1 M KOH	–	The Co doped MnO ₂ show onset potential at 0.01 V, and near four electron O	3.59	[70]
Ni-MnO ₂ nanoneedles	Hydrothermal	Nanoneedle	0.1 M KOH	–	Reduction potentials of –0.43 V, and the current densities of –1.24 mA cm ⁻²	2.33	[38]
Ni-doped MnO ₂ NPs	Co-precipitation	Nanowires	0.1 M KOH	124.4	ORR potential (V) of –0.348 V (vs. Ag/AgCl)	3.47	This work

Fig. 14 **a** The CV sketches of Ni-MnO₂ nanoparticles at different scan rates for ORR (modified GC electrode). **b** Sketch of the cathodic peak current with respect to $v^{1/2}$. **c** Sketch of the cathodic peak current with respect to v . **d** Plot of E_{pc} with respect to $\log v$

rate (V s⁻¹), transferred number of electrons, coefficient of transfer, Faraday constant, gas constant and temperature (K), respectively. The slope of E_p versus $\log v$ is used to calculate the value of an . The calculated value of an was

1.498 taking the slope of the plot (0.03948), as well as considering the value of R , T , K and F are 8.314 J/K mol, 298 K, and 96,480 C/mol, respectively. According to Bard and Faulkner, a can be computed using Eq. (7) [68];

$$\alpha = \frac{47.7}{E_p - E_{p/2}} \text{ mV} \quad (7)$$

where $E_{p/2}$ is the potential when the current is at half the peak value. Therefore, the computed value of α is 0.62. Hence, the number of electrons transferred (n) during the reduction process of Ni-MnO₂/GCE surface oxygen is computed to be 3.47. The finding shows that Ni-doped MnO₂ NPs are an active electrocatalyst with high catalytic performance towards ORR. Table 4 displays the comparison the electrochemical characteristics of recently studied MnO₂ based electrocatalysts. The surface area of the as-prepared Ni-MnO₂ nanoparticles in this study is 124.4 m² g⁻¹ which is in close agreement those reported for Ni- α -MnO₂ (52.3 m² g⁻¹) and Cu- α -MnO₂ Nanowire (83.8 m² g⁻¹). Similarly, the number of transferred electron is slightly greater than that of Cu- α -MnO₂ nanowires ($n = 3.2\text{--}3.3$) and Ni-MnO₂ nanoneedles ($n = 2.33$), which show that the enhancement of the electrochemical performance of Ni-MnO₂ nanoparticles was observed in this study.

4 Conclusions

Pure MnO₂ and Ni-MnO₂ electrocatalysts were prepared using a co-precipitation approach. The synthesized MnO₂ and Ni-doped MnO₂ electrocatalysts were analyzed using SEM, ICP-OES, FT-IR, XRD, UV-Vis, BET and TGA/DTA. Moreover, the electrochemical behaviors of the prepared catalysts were studied using LSV and CV. The characterization results demonstrated that highly active, cost-effective, and thermally stable electrode materials were achieved through simple co-precipitation approach. The XRD investigation showed that the doping of nickel promotes the formation of α and β -MnO₂ NPs. The tetragonal and hexagonal crystal arrangement of α , β , and ε -MnO₂ was verified via XRD investigation. The XRD examinations confirmed that the crystallite sizes of MnO₂ and Ni-doped MnO₂ were in the range of 2.25–6.6 nm. The morphological analyses showed that un-doped MnO₂ and 0.125 M Ni-MnO₂ have flower-like and nanowire structures with the estimated bandgap energy of 2.78 and 1.74 eV, respectively. It was also inferred that the thermal stability of the synthesized material was improved due to the incorporation of Ni on the MnO₂ framework. The Ni-doped MnO₂ NPs showed higher catalytic performance, as confirmed by LSV and CV analysis. Overall, Ni-doped MnO₂ NPs exhibited excellent catalytic activities, which might be because of enhanced electronic conductivity in the doping process. Hence, the addition of Ni dopants had influenced the physical characteristics of MnO₂ NPs and affected the catalytic performance of the pure MnO₂ NPs.

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Declarations

Conflict of interest The authors declare no conflict of interest regarding to the publication of this article.

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