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Rare earth metal (Sm)-doped NiMnO₃ nanostructures for highly competent alkaline oxygen evolution reaction

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In the present work, samarium-doped nickel manganese oxide was produced by employing a straightforward co-precipitation method. A peak with a 2θ of 36° corresponded to the (110) plane confirming the formation of the rhombohedral crystal structure of NiMnO₃. The existence of Mn–O and Ni–O stretching vibration modes was confirmed by Raman spectroscopy. FTIR spectra confirmed the existence of the metal–oxygen bond of NiMnO₃. The synthesized ternary Ni-based material was found to be spherical nanoparticles with an average diameter of 0.81 μm . The electrochemical oxygen evolution reaction (OER) performance was explored on 0.02 M samarium (Sm)-doped NiMnO₃ demonstrating outstanding OER action with low 321 mV, a low Tafel slope value (109 mV dec⁻¹), and low charge-transfer resistance (0.19 Ω). Moreover, the BET results suggest that the 0.02 M Sm-doped NiMnO₃ exhibited elevated surface area (78.78 m² g⁻¹) with a mesoporous character. Therefore, NiMnO₃ doped with high concentrations of a rare earth metal, Sm, is proposed as a suitable material for next-generation water splitting applications.

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1. Introduction

Water splitting is a spotless and sustainable approach for energy-conversion applications. Interestingly, extensive methods, such as electrochemical, photoelectrochemical, thermal and photocatalytic techniques, *etc.*, have been used for water splitting applications.^{1,2} Among the various methods, electrochemical water splitting is a user-friendly technique with unique advantages, such as zero emissions, high energy density and conversion efficiencies, *etc.*³ The main aim of water splitting techniques is to decrease the overpotential and increase the efficiency of various electrocatalyst materials.⁴ Recently, various oxides, sulfides, phosphides, nitrides, alloys, chalcogenides, *etc.* have been employed because of their high catalytic activities and natural abundance.⁵

Transition metal oxides are promising materials for various applications, such as for use in lithium-ion batteries, supercapacitors, water oxidation, hydrogen production, and urea oxidation.⁶ However, they have limited application due to their poor conductivity and insufficient active sites. Attempts have

been made to overcome these issues by various approaches, such as the incorporation of metal ions, the introduction of carbon-based materials and quantum dots, *etc.*⁷ In particular, rare earth metal-doped metal oxides exhibit excellent activities, which improve the conductivity of the material and the surface area, and enhance the diffusion paths.⁸ Numerous rare-earth metals, such as gadolinium, neodymium, dysprosium, and samarium have been used as doping agents.⁹ Among these metals, samarium dramatically improves the ionic conductivity, carrier transportability, and catalytic performance.¹⁰ In addition, nickel-based materials have gained special attention for the oxygen evolution reactions (OER) due to their benefits of lower water oxidation potential.¹¹ Many methods are now available to prepare metal oxide electrocatalysts *via* hydrothermal, co-precipitation and microwave-assisted techniques, *etc.*¹² Amongst these, co-precipitation is a less time-consuming technique performed at low temperatures.¹³

Numerous researchers have assessed the application of nickel manganese oxide (NMO) for various purposes. For example, Mustafa Al Samarai *et al.*¹⁴ synthesized a graphene-supported Ni₃MnO₄ catalyst by a reverse micellar method for electrocatalytic OER. Yan Zhang *et al.*¹⁵ synthesized a nickel manganese composite oxide nanomesh *via* the hydrothermal method, followed by high-temperature calcination for use in supercapacitors and electrochemical water oxidation. Dongxiao Ji *et al.*¹⁶ fabricated carbon-based nickel and manganese oxide nanoparticles *via* the electrospinning-calcination method for electrochemical water oxidation. In this study, NMO was

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synthesized from the co-precipitation and subsequent calcinations for the OER. Structural and morphological studies confirmed the formation of NiMnO₃ nanocomposite. In addition, the doping agent, samarium, not only changed the electrical properties of the nanocomposite but also improved the electrochemical performance of the nanocomposite material.

2. Experimental procedure

Chemical reagents, such as nickel(II) and manganese(II) nitrate [(Ni(NO₃)₂, (Mn(NO₃)₂], sodium bicarbonate (NaHCO₃), ethanol (C₂H₅OH), and methanol (CH₃OH), were procured. NMO was produced by a simple co-precipitation technique. In brief, an equal (1 : 1) molar ratio of nickel and manganese precursors was mixed and dissolved with 50 ml of deionized water. After stirring well, 1.0 M sodium bicarbonate was added; within some hours, a green-bluish precipitate appeared, which was washed with distilled water, ethanol, and methanol. The material thus obtained was transferred to the oven at 80 °C for 12 h. After drying, the product was annealed at 400 °C for 4 h. The formation of a black fine powder indicated the formation of NMO. Likewise, different concentrations of samarium (0.01 and 0.02 M)-doped NMO samples were synthesized by the above procedure using appropriate ratios of materials. The black

powder samples were labeled NMO1, NMO2, and NMO3. The electrochemical water oxidation analysis of the synthesized products was examined in three electrode workstations. In these workstations, platinum was used as a counter electrode, Ag/AgCl was used as a reference electrode. The NMO samples were employed as working electrodes with 1 M KOH as the electrolyte.

3. Results and discussion

The XRD spectra were used to examine pure NiMnO₃, as well as different concentrations (0.01, 0.02 M) of Sm-doped NiMnO₃. The diffraction peaks at 25, 34, 37, 42, 51, 55, 64, and 66° belonged to the (012), (104), (110), (113), (024), (116), (214), and (300) crystal faces of NiMnO₃. The XRD indexed peaks were well-oriented with the standard JCPDS (#00-012-0269) with the space group R. The rhombohedral crystal structure of NiMnO₃ is shown in Fig. 1A. No other characteristic peaks can be observed in Fig. 1A(b and c), indicating that the doping agent, Sm, did not introduce a second crystal phase in NiMnO₃.¹⁷ The average crystalline sizes of the synthesized products, such as NMO1, NMO2, and NMO3, were 35.53, 17.76, and 14.81 nm respectively. Fig. 1B shows Raman spectra for pure NiMnO₃ and different concentrations (0.01, 0.02 M) of Sm-doped NiMnO₃.

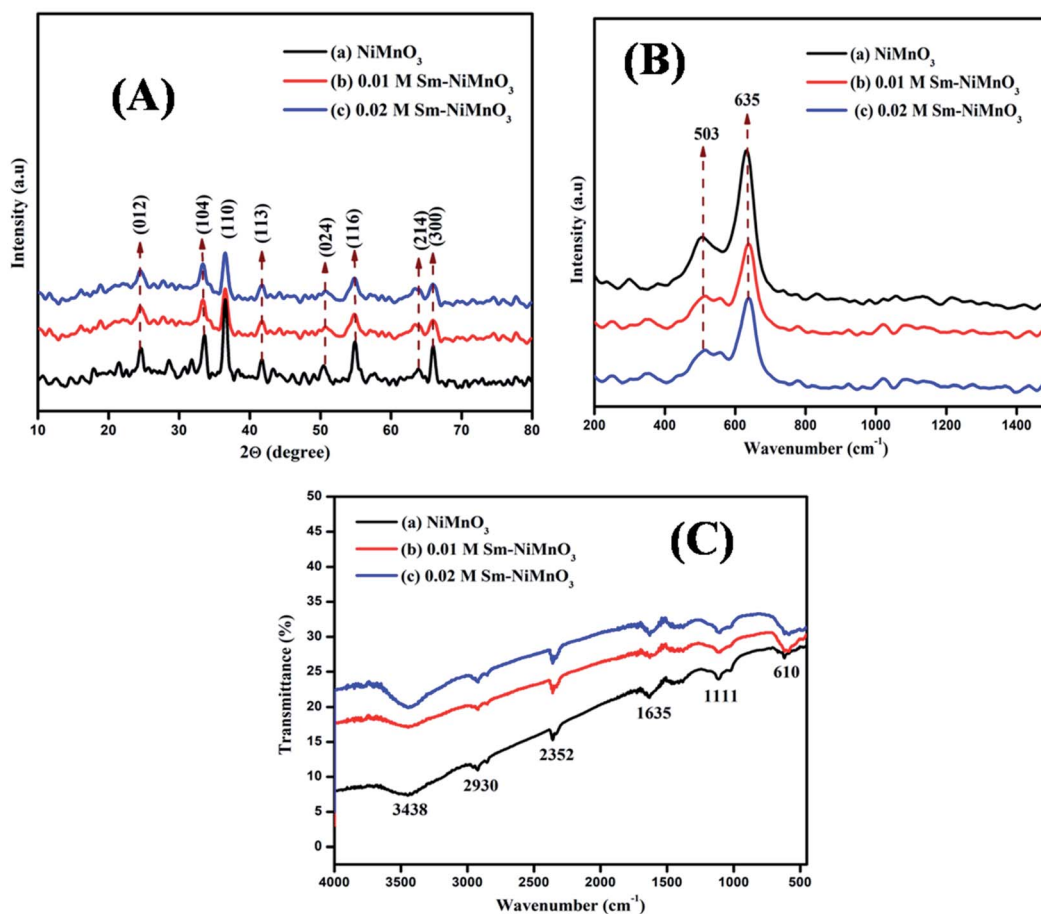


Fig. 1 (A) XRD spectra (B) Raman, and (C) FTIR spectra of pristine NiMnO₃, 0.01 M Sm-doped NiMnO₃, and 0.02 M Sm-doped NiMnO₃.

Two peaks, 503 and 635 cm^{-1} , were observed at the wave-number range from 200 to 1400 cm^{-1} . The strong band at 635 cm^{-1} revealed asymmetric Mn–O stretching and the weak band located at 503 cm^{-1} indicated Ni–O stretching.¹⁸ Fig. 1C shows the FTIR spectra of pure NiMnO₃ and different concentrations (0.01, 0.02 M) of Sm-doped NiMnO₃ structures. The absorption bands at 3438 and 1635 cm^{-1} revealed H–O–H water vibrations. The absorption bands present below 1111 cm^{-1} corresponded to NiMnO₃; the band at 610 cm^{-1} revealed a metal–oxygen NiMnO₃ bond. The bands observed at 2930 and 2352 cm^{-1} were ascribed to C–H bonds.¹⁹

Fig. 2(A–F) shows the SEM images of pure NiMnO₃ and different concentrations (0.01, 0.02 M) of Sm-doped NiMnO₃,

suggesting the particles to be in the micro range in size between 10 and 5 μm . The images revealed that the particles have a spherical shape with diameters of 2.26 μm (pure NiMnO₃), 2.0 μm (0.01 M Sm-doped NiMnO₃), and 0.81 μm (0.02 M Sm-doped NiMnO₃). These sizes were calculated using the Image J software. In a zoomed-in view, fine nanoparticles were seen to co-exist (Fig. 2B, D and F). Moreover, it was observable that the particle size of NiMnO₃ decreased from 2.26 to 0.81 μm , when the content of Sm dopant increased from 0 to 0.02 M. The agglomeration was also slightly reduced because of doping. In addition, the average particle sizes may decrease with increasing Sm concentrations, due to the existence of smaller radii. In detail, the ionic radius of Sm³⁺ was 1.08 Å and Ni³⁺ was

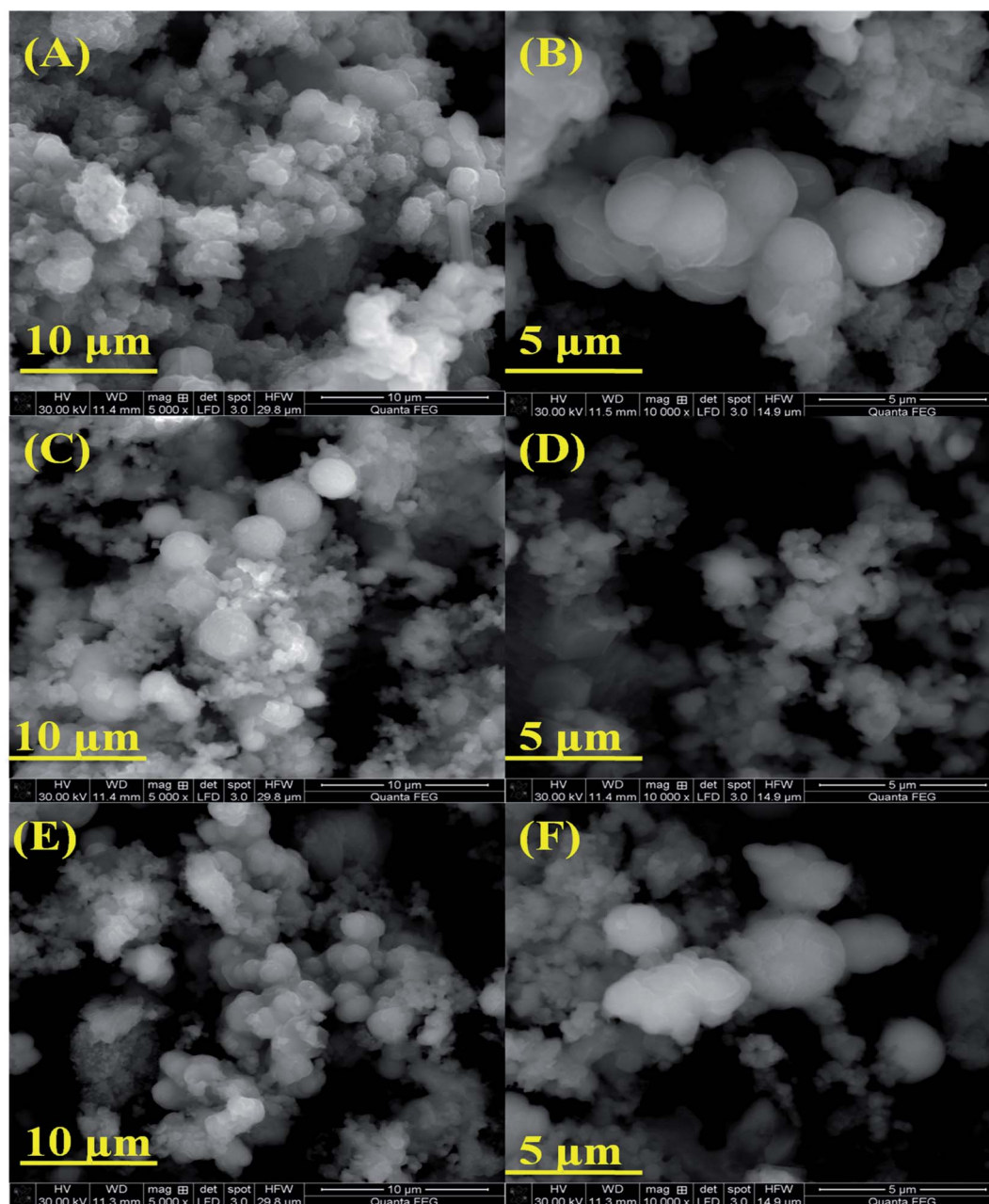


Fig. 2 SEM images (A and B) pristine NiMnO₃, (C and D) 0.01 M Sm-doped NiMnO₃, and (E and F) 0.02 M Sm-doped NiMnO₃ at 10 and 5 μm .

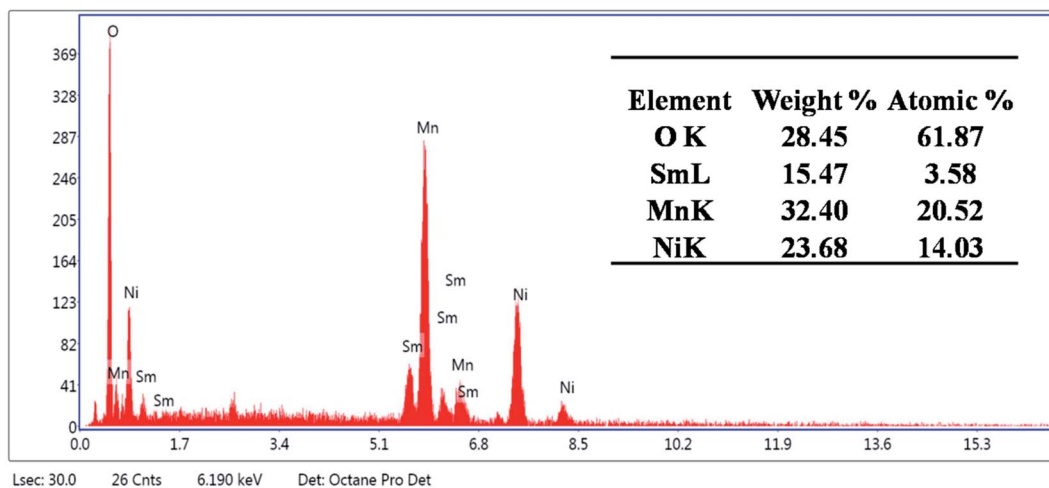


Fig. 3 An EDX spectra of 0.02 M Sm-doped NiMnO₃.

70 Å. Therefore, the radius of Sm³⁺ was very small as compared to that of Ni³⁺. Furthermore, smaller average particle sizes may be attributed due to inhibited grain growth due to the substituted Sm ions at the Ni sites. The reduced particle sizes significantly promoted the edge and corner-site contact at the catalyst surface, which enabled the formation of reaction intermediates, accelerated catalytic kinetics, and enhanced electrochemical water oxidation.^{20,21} Overall, SEM analysis suggested that increased dopant concentrations decreased the particle size, denoting that the synthesized product developed a more crystalline nature.²²

The incorporation of the doping agent, Sm, was confirmed by the EDX spectra as shown in Fig. 3. The synthesized material comprised 23.68% Ni, 32.40% Mn, 28.45% O, and 15.47% Sm by weight percentage. Moreover, the sample contained 14.03% Ni, 20.52% Mn, 61.87% O, and 3.58% Sm by atomic percentage. No other elements representing impurities were observed.

Fig. 4 shows the results of the BET surface area analysis of pure, 0.01 M, and 0.02 M Sm-doped NiMnO₃. According to the

BET studies, the surface area, pore-volume, and diameter of pure, 0.01 M, and 0.02 M Sm-doped NiMnO₃ were found and are presented in Table 1. Results revealed that 0.02 M Sm-doped NiMnO₃ had a higher surface area than other materials. Moreover, the obtained graphs depict a type IV isotherm with discrete H4 hysteresis, proving the mesoporous nature of the synthesized material. The high surface area and porous properties of the 0.02 M Sm-doped NiMnO₃ can reduce diffusion lengths, facilitating the penetration of electrolyte ions and improving the transport pathway in the electrochemical analysis.²³ Moreover, the elevated surface area offers additional

Table 1 BET analysis of the prepared materials

Materials	Surface area	Pore volume	Pore diameter
NiMnO ₃	38.065 m ² g ⁻¹	0.174 cc g ⁻¹	1.960 nm
0.01 M Sm-NiMnO ₃	44.332 m ² g ⁻¹	0.176 cc g ⁻¹	14.857 nm
0.02 M Sm-NiMnO ₃	78.78 m ² g ⁻¹	0.439 cc g ⁻¹	11.252 nm

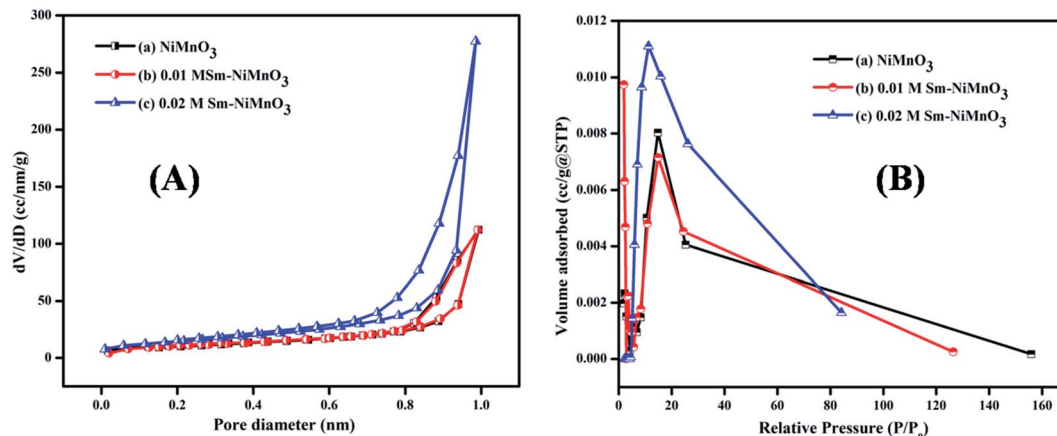


Fig. 4 (A) Nitrogen adsorption–desorption and (B) BJH pore diameter of pristine NiMnO₃, 0.01 M Sm-doped NiMnO₃, and 0.02 M Sm-doped NiMnO₃.

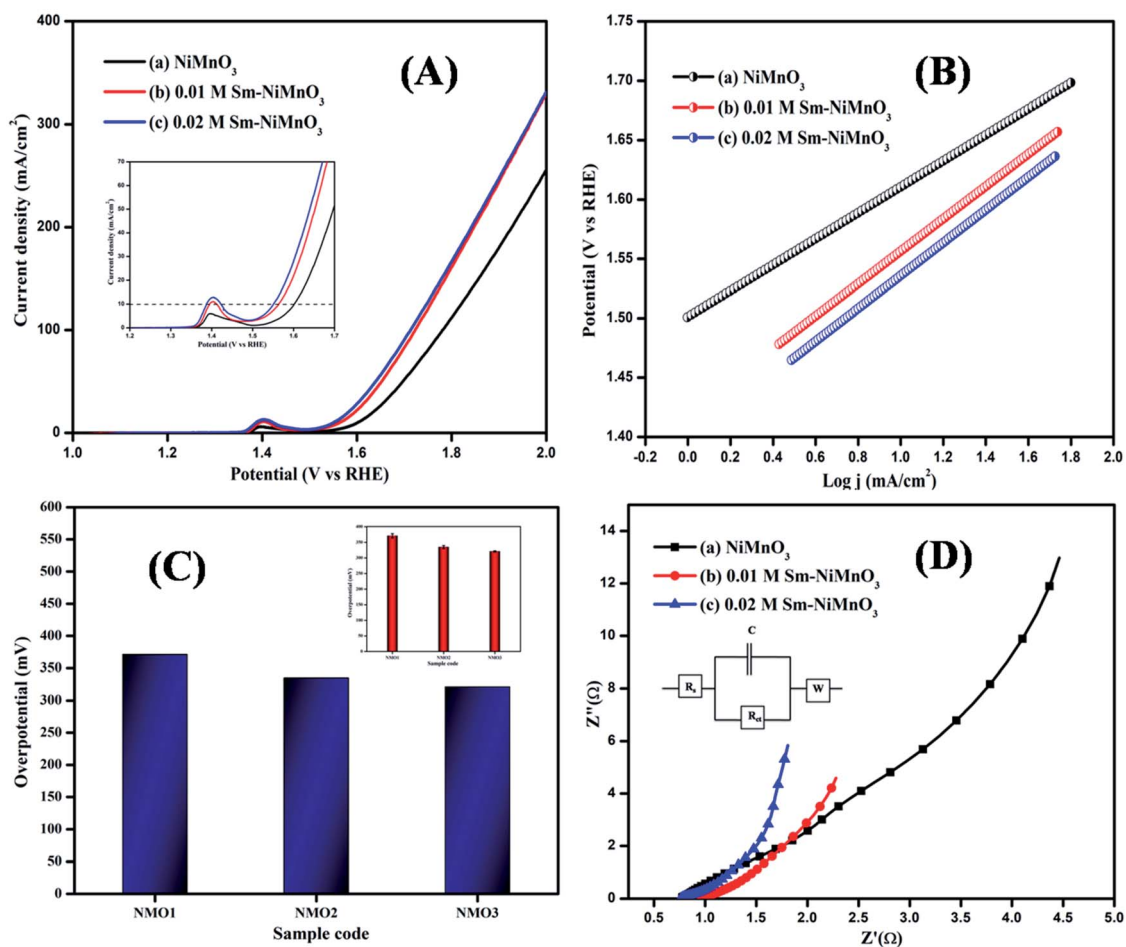


Fig. 5 (A) LSV spectra, (B) Tafel slope (C) Bar diagram (inset: error bar), and (D) EIS spectra of pristine NiMnO₃, 0.01 M Sm-doped NiMnO₃, and 0.02 M Sm-doped NiMnO₃.

active sites and helps improve electrochemical OER performance.

The LSV curves of pure, 0.01 M, and 0.02 M Sm-doped NiMnO₃ were recorded from 0 to 1 V at 2 mV s⁻¹ (Fig. 5A). The 0.02 M Sm-doped NiMnO₃ showed better OER activity and required only 321 mV to reach the benchmark of 10 mA cm⁻². Contrarily, the other electrocatalysts, such as pristine NiMnO₃ and 0.01 M Sm-doped NiMnO₃, need 371 and 335 mV to attain the same current density (Fig. 5C). Generally, Ni-based binary or

ternary materials exhibit excellent electrochemical performance than pure Ni materials.²⁴ Moreover, the rare earth dopant, Sm, also improved the surface area, further improving the OER activity. The electrode material had a larger surface area as compared to the electrocatalyst. Hence, superior electrochemical performance was expected due to the addition of Sm to NiMnO₃, which could, in turn, produce high electrochemical OER activity. A comparison of these findings with those from previous literature is tabulated in Table 2.

Table 2 A comparison of results obtained here with that of previous works

Material	Overpotential values	Tafel slope values	Ref.
NiO	396 mV	54 mV dec ⁻¹	25
NiFe ₂ O ₄ hollow fiber/Ni foam	433 mV	134 mV dec ⁻¹	26
3D NiO _x /Ni foam	390 mV	80 mV dec ⁻¹	27
NiO hollow nanofibers/Ni foam	340 mV	84 mV dec ⁻¹	28
Ni _{0.9} Fe _{0.1} O _x	340 mV	31 mV dec ⁻¹	29
MnO ₂ NSs	423 mV	79.6 mV dec ⁻¹	30
MnO ₂ NSs/Co ₃ O ₄ NPs-1:2	355 mV	56.5 mV dec ⁻¹	30
Sm-NiMnO ₃	321 mV	109 mV dec ⁻¹	[Present work]

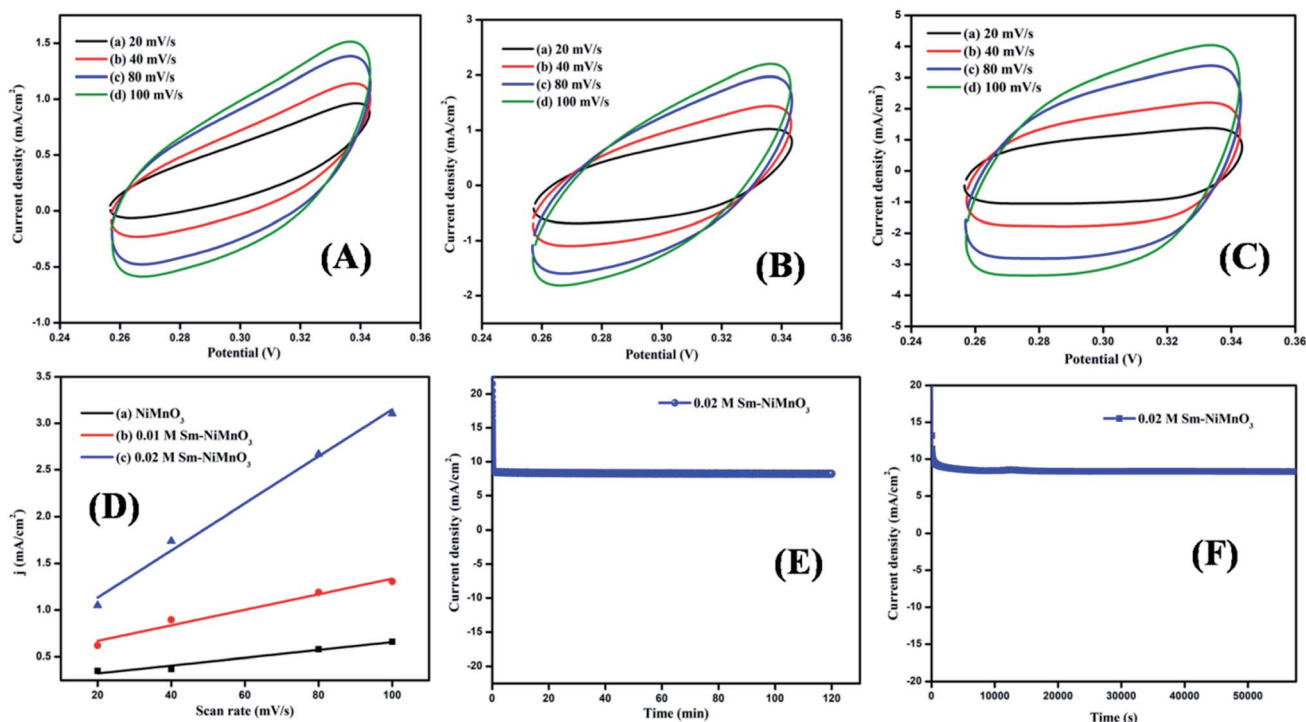


Fig. 6 (A–C) CV Curves and (D) double-layer capacitance for pristine NiMnO₃, 0.01 M, 0.02 M Sm-doped NiMnO₃, chronoamperometry test of 0.02 M Sm-doped NiMnO₃ for (E) 2 h and (F) 16 h.

Tafel slope curves were derived from the polarization curves, which were then used to investigate the material OER kinetics (Fig. 5B). Tafel slopes of 138, 136, and 109 mV/dec were obtained for pure NiMnO₃, 0.01 M, and 0.02 M Sm-doped NiMnO₃. 0.02 M Sm-doped NiMnO₃ showed a small slope of 109 mV/dec as compared to the other two materials. A low Tafel slope value denotes rapid electron transport and superb OER catalytic kinetics.³¹

The EIS analysis was performed on all prepared materials, to obtain further information on OER kinetics (Fig. 5D). 0.02 M Sm-doped NiMnO₃ presented charge transfer (R_{ct}) and solution resistance (R_s) of 0.19 and 0.76 Ω , respectively, which were smaller than those of other materials, *i.e.*, 0.01 M Sm doped NiMnO₃ ($R_s = 0.77 \Omega$, $R_{ct} = 0.20 \Omega$) and pure NiMnO₃ ($R_s = 0.96 \Omega$, $R_{ct} = 0.26 \Omega$). The fitted equivalent circuit has been inserted in Fig. 5D. These results suggest that the 0.02 M Sm-doped NiMnO₃ had more favorable OER kinetics because a low R_{ct} value denotes highly proficient charge transfer and a speedier faradaic process.³²

The electrochemical activity towards OER was further studied with the help of double-layer capacitance. The cyclic voltammogram was obtained at a potential of 0.26–0.34 V at various scan rates of 20, 40, 80, and 100 mV s^{-1} , respectively (Fig. 6(A–C)). As predicted, 0.02 M Sm-doped NiMnO₃ showed C_{dl} values of 25.2 mF cm^{-2} , whereas the 0.01 M Sm-doped NiMnO₃ and pure NiMnO₃ showed the C_{dl} values of 8.3 and 4.1 mF cm^{-2} , respectively (Fig. 5D). Moreover, the electrochemical active surface area (ECSA) was estimated following the equation: $\text{ECSA} = C_{dl}/C_s$; C_{dl} - double-layer capacitance and C_s -

sample-specific capacitance. The estimated ECSA of pure NiMnO₃, 0.01 M, and 0.02 M Sm-doped NiMnO₃ were 0.205, 0.415, and 1.26 cm^2 respectively. These results suggest that the incorporation of Sm in NiMnO₃ provided greater surface area, which could offer additional exposed surface reactive sites for OER activity.³³

A durability test for 0.02 M Sm-doped NiMnO₃ was performed using chronoamperometry (Fig. 6E and F). No further changes were observed in the current density of 0.02 M Sm-doped NiMnO₃ with 98.5% retention after 2 h (Fig. 6E). Moreover, the same electrode was tested again for 16 h, whereby it exhibited 97.6% retention, clearly suggesting the material's stability in prolonged hours (Fig. 6F). Overall, the results suggest that the introduction of Sm to NiMnO₃ imparts excellent OER activity and stability to NiMnO₃ owing to the higher surface area, electrical conductivity, and abundance of catalytic active sites in the Sm-doped material.³⁴

4. Conclusion

Different concentrations of pure and Sm-doped NiMnO₃ were synthesized by employing a low-temperature co-precipitation technique. The structures and shapes of the electrocatalysts thus produced were determined by XRD, Raman, FTIR, and SEM analyses. In addition, the existence of Sm was confirmed using EDX analysis to confirm that no other trace elements existed in the synthesized sample. Electrochemical studies showed that 0.02 M Sm-doped NiMnO₃ exhibited a high double-layer capacitance (C_{dl}) of 25.2 mF cm^{-2} and a high

electrochemically active surface area of 1.26 cm^2 . In addition, the 0.02 M Sm-doped NiMnO_3 exhibited excellent stability and OER performance at 321 mV as compared to other samples, such as pure NiMnO_3 (371 mV) and 0.01 M Sm-doped NiMnO_3 (335 mV). Therefore, the incorporation of the rare earth element, samarium (Sm), improved the surface area, charge-transfer ability, and efficacy of the catalytic active sites.

Conflicts of interest

There are no conflicts to declare.

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