

Ultrahigh density defects of Mn₃O₄ boosting oxygen evolution reaction

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Abstract. Surface defects have a positive effect on the improvement of electrocatalytic performance due to the ability to introduce half-metallicity into selected semiconductors. Herein, we prepare a defect-rich Ni-doped Mn₃O₄ (Ni-Mn₃O₄) material by a simple hydrothermal and impregnation method. Ni-Mn₃O₄ exhibits a unique morphology consisting of ultrathin nanoarrays and nanoflowers embellished at the top, which endows the material with large specific surface area and reactive sites and contributes to enhanced oxygen evolution reaction (OER). The obtained Ni-Mn₃O₄ shows improved OER activity with the overpotential of 290 mV at the current density of 20 mA cm⁻². This remarkable OER performance can be attributed to the multi-dimensional interface and ultra-high density defects, leading to the formation of abundant active sites, thereby inducing half-metallicity properties and suitable intermediate adsorption energies. This work is expected to provide reference and guidance for the design and synthesis of high-performance electrocatalysts.

Keywords: Mn₃O₄, Ni doping, defects, OER.

1. Introduction

Climate change is a major global challenge facing humanity today. In order to actively respond to climate change, carbon neutrality has become an important issue worldwide. Hydrogen energy is a clean, efficient, renewable and ideal energy source, which can be efficiently converted into electricity and is regarded as one of the most promising energy sources. Hydrogen production by water electrolysis is an important approach to achieving industrial production of green hydrogen [1,2]. The sluggish kinetics of oxygen evolution reaction (OER), a crucial half-reaction of water electrolysis, hinders the improvement of reaction efficiency[3]. Therefore, the search for inexpensive, abundant and excellent OER catalysts has become a hot research topic in recent years. Compared with noble metal catalysts, 3d transition metal oxides with higher practical value have more electronic freedom to regulate the kinetics of OER reaction[4].

The Manganese-based oxides are appealing materials for OER owing to the wide range of oxidation states[5], such as MnO₂, Mn₃O₄, Mn₂O₃ and MnO, however, they have not been studied as intensively as FeCoNi. Among them, the spinel Mn₃O₄ exhibits favorable electrical conductivity due to the excellent electron transfer between oxidation states +2 and +3 [6]. The origin of the active sites of OER in Mn₃O₄ has been thoroughly investigated by Tiwari and his teams. They confirmed by experiments and theoretical calculations that it is the Mn(III) site present on the (112)-oriented surface of Mn₃O₄ that is highly active for OER[7]. Actually, the

conductivity and the number of active sites cannot be enhanced enough for electrocatalysts, which can be realized by defect construction and atomic doping[8-11]. For example, Zhou et al. induced lattice distortion of Mn₃O₄ by Ni doping, which also led to the production of distorted octahedral Mn(III) species and increased the number of active sites in the OER[8]. Nevertheless, the electrocatalytic OER activity of Mn₃O₄ is still far behind that of precious metals and transition metals such as Fe and Ni, and it is necessary to further improve the electrochemical performance.

Herein, we have successfully prepared spinel Mn₃O₄ on nickel foam (NF) by a novel in situ growth process and realized Ni doping on Mn₃O₄ (Ni-Mn₃O₄) via a sample dipping. The obtained Ni-Mn₃O₄ exhibits outstanding OER activity in alkaline media. The overpotential required at 20 mA cm⁻² is 290 mV. The higher catalytic activity can be attributed to the unique multidimensional structure with two-dimensional nanoflowers dotting with one-dimensional nanosheets. Such morphology can expose abundant active Mn³⁺ sites and provide large active surface area. Besides, the ultrahigh density defects also contribute to the increase of active center and conductivity. This defect-engineering and atom doping strategy provide a feasible approach for the large-scale development of Mn-based material.

2. Experimental Section

2.1 Synthesis of Mn_3O_4

Mn_3O_4 was synthesized using a simple hydrothermal method. 2 mmol of KMnO_4 was dissolved in 40 ml of deionized water under mechanical stirring. The resulting dark purple solution was then transferred to a 50 ml Teflon-lined autoclave containing a clean piece of NF (1 cm $\times$ 4 cm) (0.11 g). The autoclave was then heated at 180 $^\circ\text{C}$ for 3 hours. After natural cooling to room temperature, the samples were washed several times with deionized water and ethanol and then dried in a vacuum drying oven.

2.2 Synthesis of $\text{Ni}_x\text{-Mn}_3\text{O}_4$

The above Mn_3O_4 was dipped into the 20 ml solution containing x M ($x=0.05, 0.15$ and 0.20) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for 2 h at 80 $^\circ\text{C}$. The prepared $\text{Ni-Mn}_3\text{O}_4$ was washed with deionized water and dried for later use.

2.3 Characterization

X-ray diffraction (XRD) was performed on a Bruker D8 Advanced X-ray diffractometer Cu $\text{K}\alpha$ radiation ($\lambda=0.1542$ nm). Scanning electron microscopy (SEM) images were obtained via the JEM 2011 F equipment. Transmission electron microscopy (TEM) images and related element mapping were detected via the FEI Tecnai G20 device. X-ray photoelectron spectroscopy (XPS) was detected on Thermo Scientific Escalab 250 photo-electron spectrometer.

2.4 Electrochemical measurements

Electrochemical measurement was performed on Gamry 3000 workstation using a three-electrode system in 1.0 M KOH. The obtained samples, Pt wire and saturated calomel electrode are chosen as work electrode, counter electrode and reference electrode, respectively. All the potentials were converted to reversible hydrogen electrode (RHE) according to the Nernst equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.2415 + 0.0592\text{pH}$. Polarization curves were collected with a scan rate of 5 mV s^{-1} . The electrochemical impedance spectroscopy (EIS) was measured under an open circuit potential from 0.1 Hz to 100 Hz at the current voltage amplitude of 5 mV. Chronopotentiometric method was used to test the stability of electrocatalysts at 10 mA cm^{-2} .

3. Results and discussion

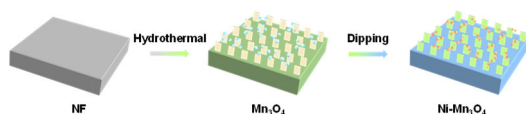


Figure 1: Schematic diagram of the preparation process of Ni-doped Mn_3O_4 .

As shown in Figure 1, $\text{Ni-Mn}_3\text{O}_4$ was synthesized by a simple hydrothermal reaction and subsequent solution impregnation. Firstly, the color of NF changed from silver

to black during the hydrothermal treatment in the KMnO_4 solution. Subsequently, the Ni-doped Mn_3O_4 was fabricated by immersing the obtained Mn_3O_4 in an aqueous solution containing Ni^{2+} ions.

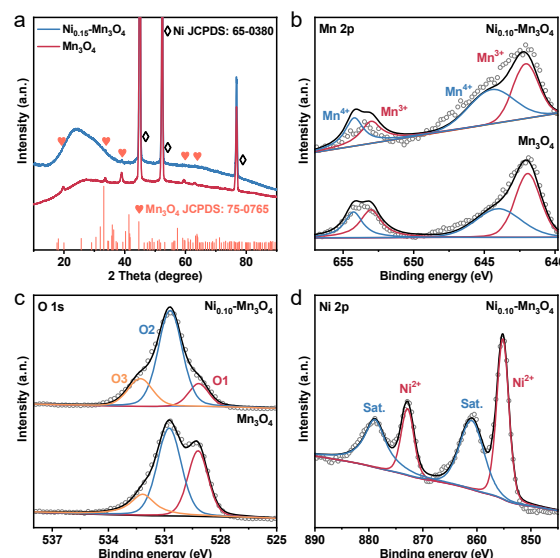


Figure 2: (a) XRD of Mn_3O_4 and $\text{Ni-Mn}_3\text{O}_4$. (b) Mn 2p, (c) O 1s and (d) Ni 2p of $\text{Ni-Mn}_3\text{O}_4$.

The crystal structures of Mn_3O_4 and $\text{Ni-Mn}_3\text{O}_4$ were investigated by XRD. As presented in Figure 2a, in addition to the three strong peaks at 44.9° , 52.5° and 76.9° belonging to metallic Ni (JCPDS: 65-0380), the characteristic peaks of the (020), (023), (041), (152) and (153) crystal planes of orthorhombic Mn_3O_4 (JCPDS: 75-0765) can be observed at 18.7° , 33.5° , 38.9° , 59.4° , 63.1° , respectively. After being treated in Ni^{2+} solution for 2 h, no Ni-related peaks can be discerned. Besides, these peaks shift to higher degree and become weaker, indicating that Ni atom has been successfully introduced and that the incorporation of Ni leads to the generation of more defects. Further, XPS was applied to identify the chemical properties and composition of the surface of Mn_3O_4 and $\text{Ni-Mn}_3\text{O}_4$ samples. In Mn 2p region (Figure 2b), the peaks located at 642.0 and 652.9 eV can be assigned to Mn^{3+} , and another set of peaks at 644.5 and 654.2 eV come from the Mn^{4+} species. It is noted that the atomic ratio $\text{Mn}^{3+}:\text{Mn}^{4+}$ of Mn_3O_4 was about 1.15, which is higher than that of $\text{Ni-Mn}_3\text{O}_4$ (1.12). The increase in active Mn^{3+} content will inevitably and dramatically encourage the enhancement of OER activity. O 1s XPS is composed of three peaks located at 529.2 (O1), 530.7 (O2) and 532.1 eV (O3), resulting from lattice oxygen, defective oxygen and absorbed oxygen on the surface, respectively. Furthermore, as shown in Figure 2d, the Ni 2p spectrum consists of four peaks, where the peaks at 854.9 and 872.7 eV are related to the Ni $2p_{3/2}$ and $2p_{1/2}$ of Ni^{2+} ions. Additionally, the satellite peaks situated at 860.8 and 878.9 eV also verify the presence of Ni^{2+} .

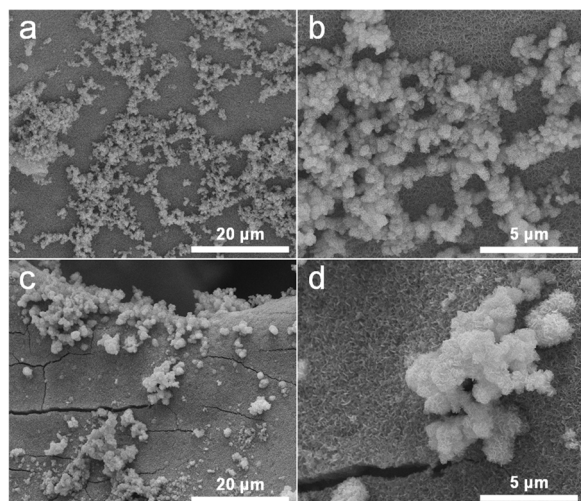


Figure 3: SEM images of (a,b) Mn_3O_4 and (c,d) $\text{Ni-Mn}_3\text{O}_4$.

To check the morphology of Mn_3O_4 and $\text{Ni-Mn}_3\text{O}_4$ samples, SEM images were detected and displayed in Figure 3. For Mn_3O_4 , it can be clearly observed that the nanosheet arrays densely distribute over the entire NF, dotted with nanoflower microspheres with a diameter of ~ 450 nm. The coupling of one- and two-dimensional structures undoubtedly greatly increases the electrochemically active specific surface area, exposing an abundance of active sites. The structure of the nanosheets and nanoflowers after the impregnation treatment did not change significantly except that the surface became rough and the diameter of the nanoflowers expanded to ~ 1000 nm. This transition will further stimulate the reactivity by increasing the surface area.

In addition, Figure 4a gives the high-resolution TEM (HRTEM) images, proving the generation of ultrahigh density defects for $\text{Ni-Mn}_3\text{O}_4$. The existence of a large number of dislocations and lattice mismatches can modulate the catalyst energy band structure and adsorption properties of the material, which is expected to further drive the OER performance enhancement. The insertion in Figure 4a is the high-angle annular dark field (HAADF) image, confirming the lamellar structure with wavy folds. The corresponding element mappings are also collected, suggesting the homogenous dispersion of Ni, Mn and O in the ultrathin $\text{Ni-Mn}_3\text{O}_4$ nanosheets.

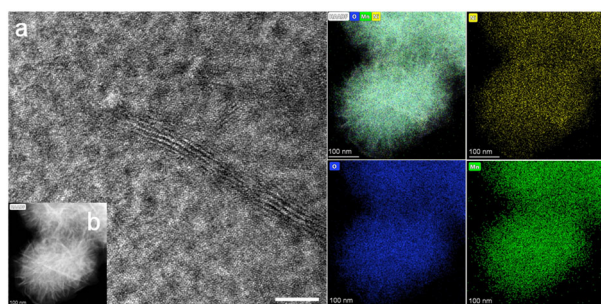


Figure 4: (a) HRTEM image and (b) HAADF image and corresponding element mapping of $\text{Ni-Mn}_3\text{O}_4$.

As discussed above, the ultrahigh density defects and large surface area would be propitious to water oxidation. Therefore, the electrochemical OER performance of

synthesized samples was measured in alkaline media using a standard three-electrode system. As shown in Figure 5a, all the samples exhibit OER activity higher than commercial RuO_2 . The Ni^{2+} content was first optimized and the maximum promotion effect was observed when the Ni^{2+} concentration in the solution was 1.0 M, conferring the highest OER activity to $\text{Ni}_{0.10}\text{-Mn}_3\text{O}_4$. At the current density of 20 and 50 mA cm^{-2} , the needed overpotential is 290 and 353 mV, which is a 52 mV (50 mA cm^{-2}) reduction from the Mn_3O_4 precursor.

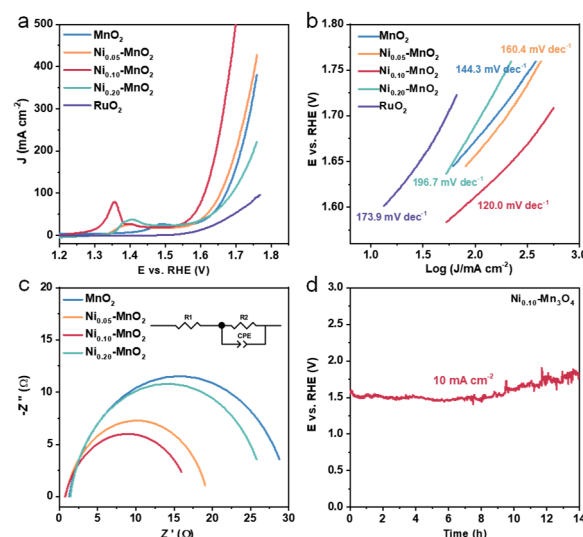


Figure 5: Electrocatalytic OER performances of the samples. (a) polarization curves, (b) Tafel plots, (c) EIS and (d) v - t curves at 10 mA cm^{-2} .

Moreover, the Tafel slopes were also calculated by fitting the polarization curves to study the reaction kinetics (Figure 5b). The Tafel slope of $\text{Ni}_{0.10}\text{-Mn}_3\text{O}_4$ is $120.0 \text{ mV dec}^{-1}$, lower than Mn_3O_4 ($144.3 \text{ mV dec}^{-1}$) and other contrast samples. Such result indicates Ni doping expedites the catalytic kinetics of Mn_3O_4 . Moreover, in order to gain deeper insight into the excellent OER activity, EIS studies were carried out and the measured impedance data was fitted according to an equivalent electrical circuit (inset of Figure 5c). The R_1 , R_2 and CPE represent electrolyte solution resistance (R_s), charge-transfer impedance (R_{ct}) and constant phase angle components associated with electric double layer capacitance. Encouragingly, $\text{Ni}_{0.10}\text{-Mn}_3\text{O}_4$ also possesses the smallest impedance with the R_{ct} of 16.4Ω , lower than Mn_3O_4 (28.8Ω) $\text{Ni}_{0.05}\text{-Mn}_3\text{O}_4$ (18.2Ω) $\text{Ni}_{0.20}\text{-Mn}_3\text{O}_4$ (25.5Ω), which implies that $\text{Ni}_{0.10}\text{-Mn}_3\text{O}_4$ owns a high electrical conductivity and fast transfer rate. Given that operational stability is a critical indicator for electrocatalysts, we further analyzed the long-term stability of the best-performing $\text{Ni}_{0.10}\text{-Mn}_3\text{O}_4$. The v - t curve shows that $\text{Ni}_{0.10}\text{-Mn}_3\text{O}_4$ can run stably for at least 14 h at the constant current density of 10 mA cm^{-2} , confirming the excellent durability. In a nutshell, the ultrahigh density defects and multiscale structure endow $\text{Ni}_{0.10}\text{-Mn}_3\text{O}_4$ with boosted catalytic performance for OER.

4. Conclusion

In summary, the Ni-doped Mn₃O₄ nanosheet arrays have been successfully prepared through an in situ growth method and impregnation method. The obtained Ni_{0.10}-Mn₃O₄ delivers the current density of 20 mA cm⁻² at 290 mV. The superior OER activity would result from the following two factors. Firstly, the ultrahigh density defects and Ni doping reinforce electron transfer and surface adsorption. Secondly, the coupling of one-dimensional nanosheets and two-dimensional nanoflowers enlarges the active surface area and exposes more active catalytic sites. In addition, such a structure facilitates sufficient contact between the Ni_{0.10}-Mn₃O₄ catalyst and electrolyte. This work pinpoints the potential of defect engineering and atom doping in the development of earth-abundant elemental electrocatalysts for water oxidation.

Acknowledgements

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