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1 Ligand-mediated Tailoring of Self-supported $Mn_xO_y@Ni(OH)_2$
2 Nanoheterostructures with Enhanced OER Performance

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22 **Keywords:** nickel hydroxide, manganese oxide, layer structures, oxides structures, colloidal
23 nanoparticle, oxygen evolution reaction.

Abstract

We report a colloidal synthesis strategy for producing $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ nanoheterostructures under mild conditions, i.e. low temperature and ambient pressure. The role of carboxylic acid ligands in directing the synthesis is systematically explored, revealing that lower ligand concentrations along with low-molecular weight molecules favor the formation of well-defined $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ heterostructures. Electrochemical characterization demonstrates that the resulting nanocomposites exhibit significantly enhanced electrochemical surface area and oxygen evolution reaction (OER) activity compared to their single-component counterparts. Specifically, $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ achieves a low overpotential of 299 mV at 10 mA cm^{-2} , a Tafel slope of 61 mV dec^{-1} , and a low charge transfer resistance of 9 Ω . The improved OER performance is attributed to the synergistic effect between the $\text{Ni}(\text{OH})_2$ nanosheets, which facilitate $^*\text{OOH}$ intermediate formation, and the MnO_2 component, known for its intrinsic catalytic activity. Additionally, Mn_3O_4 serves as a stabilizing phase and precursor to MnO_2 , contributing to the overall durability and structural integrity of the catalyst.

1. Introduction

The oxygen evolution reaction (OER) is a key electrochemical process that dictates the efficiency of various renewable energy technologies, including water electrolysis, metal-air batteries, and regenerative fuel cell.^[1-7] However, as a multi-electron, kinetically sluggish reaction, OER often represents the rate-limiting step in these systems. To overcome this challenge, efficient catalysts are required to reduce the overpotential and accelerate reaction kinetics. Developing highly active, stable, and cost-effective OER catalysts is essential for advancing sustainable energy conversion and storage technologies.^[8-14]

Noble metals such as Pt and Au, along with metal oxides like RuO_2 and IrO_2 , exhibit excellent catalytic activity and chemical stability for OER.^[15-17] However, their high cost and scarcity have driven research efforts toward more economical and widely available alternatives. Transition metal (TM)-based catalysts, including Mn, Ni, Co, Cu, Zn, and Ti, have emerged as promising alternatives, with optimized formulations achieving electrochemical performances comparable to noble metals.^[18,19]

1 Among transition metal catalysts, Mn and Ni have attracted significant attention for OER
2 applications. Mn-based oxides are particularly promising for water oxidation, drawing inspiration
3 from the natural OER mechanism in photosystem II (PSII). [20,21] In biological systems, OER is
4 facilitated by a Mn_4CaO_5 cluster, stabilized by surrounding amino acid residues, achieving an
5 impressively low OER overpotential (η_{OER}) of 150–300 mV. [22,23] Synthetic manganese oxides
6 (Mn_3O_4 , MnO_2 , MnO) exhibit reversible redox cycling among Mn^{2+} , Mn^{3+} , and Mn^{4+} oxidation
7 states, making them excellent electronic regulators for enhancing the catalytic performance of
8 other elements, such as Ni. [24–30]

9 Similar to Mn, Ni has been identified as a highly active OER catalyst, primarily due to its strong
10 interaction with hydroxyl-adsorbed species and its ideal $\text{Ni}^{3+}[(t_{2g})^6(e_g)^1]$ electronic configuration,
11 which facilitates efficient oxygen-related adsorption and reactivity. [31,32] This intrinsic reactivity
12 is considered a key factor for designing effective OER catalysts. [33] Notably, the electrochemical
13 performance of Mn_xO_y and $\text{Ni}(\text{OH})_2$ -based materials achieves an OER overpotential of around 370
14 mV at 5 mA cm^{-2} . [34–40]

15 Inspired by the potential synergies between Ni and Mn-based oxides in this study, we developed
16 $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ nanocomposites using a simple colloidal-based synthesis conducted under low-
17 temperature and ambient conditions. A comprehensive electrochemical evaluation of these
18 nanoheterostructures was performed, with a specific focus on correlating their OER activity with
19 the structure. By carefully optimizing synthetic parameters, such as the type and quantity of
20 carboxylic acid ligands, we achieved a controlled synthesis of self-supported $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$
21 nanoheterostructures. This configuration led to notable improvements in the electrochemical
22 performance of $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ for OER applications, demonstrating its potential as a cost-
23 effective and scalable catalyst.

24 2. Experimental section

25 **2.1. Materials:** Manganese(II) acetate ($\text{Mn}(\text{Ac})_2$, 98%), nickel(II) acetate ($\text{Ni}(\text{Ac})_2$, 99%),
26 oleylamine (OLA, 98%), oleic acid (OA, 90%), lauric acid (LA, 99%), and xylenes ($\text{C}_6\text{H}_4(\text{CH}_3)_2$,
27 98.5%) were purchased from Sigma-Aldrich. Potassium hydroxide (KOH, 85%), acetonitrile
28 anhydrous (CH_3CN , 99.8%) and nitric acid (HNO_3 , 70%) were obtained from Thermo Scientific.
29 Tetrafluoroboric acid (HBF_4 , 48% w/w) was purchased from Alfa Aesar. Caprylic acid (CA, 98%)
30 and sulfuric acid (H_2SO_4 , 98%) were purchased from Fluka. Ethanol ($\text{C}_2\text{H}_5\text{OH}$), Isopropanol

(C₃H₇OH), chloroform (CHCl₃) and hexane (C₆H₁₄) were of analytical grade and obtained from Lestlab delivering solutions L.U Mili-Q water (18 MΩ/cm) was supplied by the PURELAB flex from ELGA. All the chemical reagents were used without any additional purification, except for the multiwall carbon nanotubes (MWCNT).

Carbon cloth (CC) and MWCNT were purchased from Carnd-China. MWCNT underwent purification by being mixed with HNO₃/H₂SO₄ (3:1) and subjected to sonication for 1 hour. The resulting mixture underwent multiple cycles of precipitation and dispersion using Milli-Q water and ethanol until the supernatant solution reached a pH of approximately 7. Subsequently, they were dried at 60 °C for 24 hours.

2.2. Synthesis of Mn_xO_y nanoparticles: All the experiments were conducted in 50 mL three-neck flasks equipped with a water-cooled condenser and magnetic stirring, under room conditions (Figure S1). 170 mg of Mn(Ac)₂, and 15 mL of xylenes were mixed in a 50 mL three-neck flask and stirred for 10 min. Subsequently, 2.5 mmol of OLA (1 mL) and 2.5 mmol of OA (0.8 mL) were introduced to the mixture. The resulting solution was heated to 100 °C (at a heating rate of 5 °C/min) and then 1 mL of Mile-Q water was injected. The reaction was kept at 100 °C for 3 hours. The mixture was allowed to cool down naturally and then as-synthesized nanoparticles were washed 3 times using isopropanol and chloroform as precipitating and dispersing agents, respectively. It should be noted that this experimental procedure was adapted from previous reports and modified by the inclusion of different ligands and precursors.^[41,42]

To remove the excess organic ligands, the nanoparticles were dispersed in 10 mL of hexane, and then 0.1 mL of HBF₄ dissolved in 10 mL of acetonitrile was added. The nanoparticles solution was sonicated for 10 minutes and collected through precipitation by adding 10 mL of hexane, followed by centrifugation of the solution at 7500 rpm for 3 min. The supernatant was discarded, and the dark brownish precipitate was re-dispersed in 5 mL of ethanol. The precipitation redispersion procedure was repeated three times. Finally, the as-synthesized nanoparticles were dried under an argon flow for 10 min and stored in a sealed vial for further testing.

2.3. Synthesis of Mn₃O₄@Ni(OH)₂ nanocomposite: The synthesis was carried out by the same procedure described above, but including 120 mg of Ni(Ac)₂ into the initial solution (consisting of Mn(Ac)₂, OLA, OA and xylenes).

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2.4. Synthesis of $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ nanoheterostructures: To synthesize the $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ Nanocomposite, the amount of OA was reduced from 2.5 mmol to 1 mmol keeping the other conditions constant (method detailed above). Additionally, OA was substituted with either LA or CA while maintaining the same amount (i.e. 1 mmol).

2.5. Structural and chemical characterization: The samples were characterized through transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using a Tecnai F20, operating at 200 kV with a point-to-point resolution of 0.19 nm. Sample preparation involved drop-casting of diluted solutions of nanoparticles onto a carbon-coated copper grid (200 mesh, TED PELLA, INC.). Images were analyzed using Gatan Digital Micrograph software. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was combined with electron energy loss spectroscopy (EELS) in the Tecnai F20 by using a Gatan Quantum energy filter. Images and elemental mapping were measured in a spherical aberration-corrected transmission electron microscope FEI Titan G2 80-200 Chemi STEM with four energy-dispersive X-ray spectroscopy (EDX) detectors, operated at 80 and 200 keV. The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) patterns obtained from a Bruker AXS D8 Advance X-ray diffractometer with Ni-filtered (2 μm thickness) $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 mA and 40 kV. Scanning electron microscopy (SEM) images were obtained using a ZEISS Auriga microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) detector operating at 20 kV. The samples were prepared by dispersing the nanoparticles in ethanol, and the dilute solution was drop-casted onto silicon substrates placed on aluminum specimen mount with carbon tape. The elements chemicals states were analyzed by X-ray photoelectron spectroscopy (XPS) on a SPECS system equipped with an Al anode XR50 source operating at 150 W and a Phoibos 150 MCD-9 detector. The pressure in the analysis chamber was always below 10^{-7} Pa . The area analyzed was about $2 \times 2 \text{ mm}$. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. Data processing was performed with the Multipak data reduction software (Physical Electronic-PHI, Inc., EE. UU.). Binding energy (BE) values were corrected using the C 1s peak at 284.8 eV. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed using Shimadzu ICPE-9820 simultaneous ICP atomic emission spectrometers.

2.6. Electrochemical characterization: All electrochemical measurements were conducted at room temperature using a model CHI760E electrochemical workstation (Shanghai Chenhua

Instrument Co. Ltd., China) within a standard three-electrode cell. A platinum mesh served as the counter electrode, while a Hg/HgO electrode was utilized as a reference. The reference electrode potential was converted to RHE using the provided equation (Equation 1).^[43,44]

$$E_{\text{RHE}} = E_{\text{applied}} + E_{\text{Hg/HgO}} + (0.059 \times \text{pH}) \quad (1)$$

For the working electrode preparation, a 250 μL ink solution was aerosol-deposited onto both sides of a CC (14 x 10 mm), supported on a heating plate at 60 $^{\circ}\text{C}$. The ink solution was prepared by dispersing 3 mg of nanoparticles and 1 mg of MWCNT in 750 μL of isopropanol. Subsequently, 220 μL of Milli-Q water and 30 μL of 5% wt Nafion were added to the mixture. The resulting solution was sonicated for 1 hour to ensure homogeneity. Electrochemical tests were carried out using 1 M of KOH solution (pH=13.8) as electrolyte. Linear sweep voltammetry (LSV) measurements were performed in 1M KOH with a scan rate of 5 mV/s covering a potential range from 1 to 1.6 V vs RHE in the anodic direction. Tafel slopes were extracted from LVS curves by transforming the current axes into logarithm and potential axes into overpotential, considering a range potential of ± 20 mV around η_{OER} . Electrochemical impedance spectroscopy (EIS) tests were recorded using the overpotential value obtained from LVS. The frequency window was set from 10^5 to 0.1 Hz, and a potential amplitude of 5 mV was employed.

Cyclic voltammetry (CV) was performed at various scan rates (10, 20, 40, 60, 80, 100 mV/s) with a ± 50 mV range centered around the open circuit potential (OCP, non-faradaic region). The electrochemical double-layer capacitance (C_{dl}) was calculated from the CV data by plotting a graph of the subtraction of anodic and cathodic charge currents (Δi , Equation 2) against scan rate (v). This plot exhibited a linear correlation, and the slope of this line corresponds to the C_{dl} , as described by Equation 3).^[44]

$$\Delta i(\text{A}) = \left(\frac{i_{\text{anodic}} + i_{\text{cathodic}}}{2} \right)_{\text{OCP}} \quad (2)$$

$$\text{Slope} = C_{\text{dl}}(\text{F}) = \frac{\Delta i(\text{A})}{v(\text{V/s})} \quad (3)$$

The electrochemical surface area (ECSA, Equation 4) was calculated using the specific charge density (C_s) reported for a 1 M of NaOH solution ($40 \mu\text{F}/\text{cm}^2$).^[44,45]

$$\text{ECSA}(\text{cm}^2) = \frac{C_{\text{dl}}(\mu\text{F})}{C_s(\mu\text{F cm}^{-2})} \quad (4)$$

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Surface coverage (Γ^*) and diffusion coefficient (D) parameters of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox species were determined from CV curves recorded at different scan rates, using Equations 5 and 6, respectively.

$$i_p = \left(\frac{n^2 F^2}{4RT} \right) A \Gamma^* v \quad (5)$$

$$i_p = 2.69 \times 10^5 n^{3/2} D^{1/2} v^{1/2} CA \quad (6)$$

Here, i_p represents the average current at the redox peaks in the CV curve, A is the geometric surface area of the electrode (1 cm^2), n is the number of electrons transferred (assumed to be 1 for the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox process), F is the Faraday constant ($96,845 \text{ C mol}^{-1}$), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the absolute temperature (298 K).^[46]

The stability of the MnNi-1CA electrode was evaluated by chronoamperometry in 1.0 M KOH solution at room temperature. A constant potential of 1.6 V vs. RHE , corresponding to the onset potential for oxygen evolution, was applied, and the current response was monitored over 24 hours. Additionally, a second chronoamperometric test was performed at 1.7 V vs. RHE , a value chosen above the overpotential associated with OER activity, to assess the material's performance under more demanding electrochemical conditions.

2.7. Computational method: Spin-polarized density functional theory (DFT) calculations were performed using the Vienna ab initio Simulation Package (VASP) with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional.^[47] The core electrons were treated with Projector augmented wave (PAW) pseudopotentials.^[48] The Hubbard U approach (DFT + U) was adopted to describe the Coulomb correlation for the Ni with $U-J=5.5 \text{ eV}$, and for the Mn with $U-J=3.9 \text{ eV}$.^[49,50] A cutoff energy of 520 eV was used for the plane-wave basis set and a threshold of self-consistent-field energy convergence was $1 \times 10^{-5} \text{ eV/atom}$. The convergence criterion for the structural optimizations was a maximum force of $0.03 \text{ eV/\AA}$. The k-point meshes were $3 \times 3 \times 1$ with the Monkhorst-Pack method since the supercell is large enough.^[51]

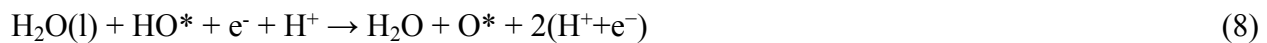
A Mn_3O_4 supported NiOOH was constructed to represent the $\text{NiOOH}/\text{Mn}_3\text{O}_4$ composite, while a heterostructure consisting of Mn_3O_4 and MnO_2 with oxygen vacancies supported on NiOOH was

used to describe the NiOOH/Mn₃O₄-MnO₂ catalyst. A vacuum layer of 15 Å thickness was used in the z-direction to eliminate the interaction between the surfaces in the slab models.

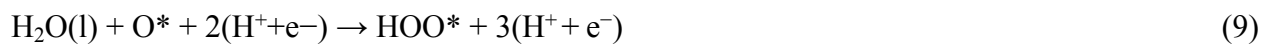
During the structure optimization, the two bottom atomic layers of manganese oxide were fixed and all other atoms were fully relaxed. The OER consists of four elementary reaction steps, and the computational hydrogen electrode (CHE) model proposed by Nørskov was used to calculate the Gibbs free energy according to the following equations. [52]



$$\Delta G_1 = \Delta G_{\text{HO}} - \Delta G_{\text{H}_2\text{O}} - eU$$



$$\Delta G_2 = \Delta G_{\text{O}} - \Delta G_{\text{HO}} - eU$$



$$\Delta G_3 = \Delta G_{\text{HOO}} - \Delta G_{\text{O}} - eU$$



$$\Delta G_4 = \Delta G_{\text{O}_2} - \Delta G_{\text{HOO}} - eU$$

ΔG_1 , ΔG_2 , ΔG_3 , ΔG_4 are the free energy changes of the four reaction steps in OER. The symbol * means the clean catalysts. HO*, O* and HOO* represent the adsorbed intermediates HO, O and HOO on the catalysts, respectively.

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \Delta G_{\text{U}} + \Delta G_{\text{pH}} \quad (11)$$

ΔE was the adsorption energy of various adsorbed intermediates obtained from DFT calculations. ΔZPE is the change of zero-point energy, T is the temperature, ΔS is the difference in entropy, and the entropy energy contributions were neglected here. When $\text{pH} = 0$, $T = 298 \text{ K}$, $P = 1 \text{ bar}$, and the electrode potential (U) was zero, the chemical potential for $(\text{H}^+ + \text{e}^-)$ was equal to that of $1/2 \text{ H}_2$ gas phase. In addition, $\Delta G_{\text{U}} = -eU$, where U was the potential of the electrode relative to the standard hydrogen electrode. In this work, the calculation condition was set to $\text{pH} = 0$, thus the correction value ΔG_{pH} can be ignored. Moreover, the overpotential η of the electrocatalyst was determined by equation (6) :

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$$\eta = \max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \} / e - 1.23 \text{ V} \tag{12}$$

Results and discussion

2.8. Structural and chemical characterization

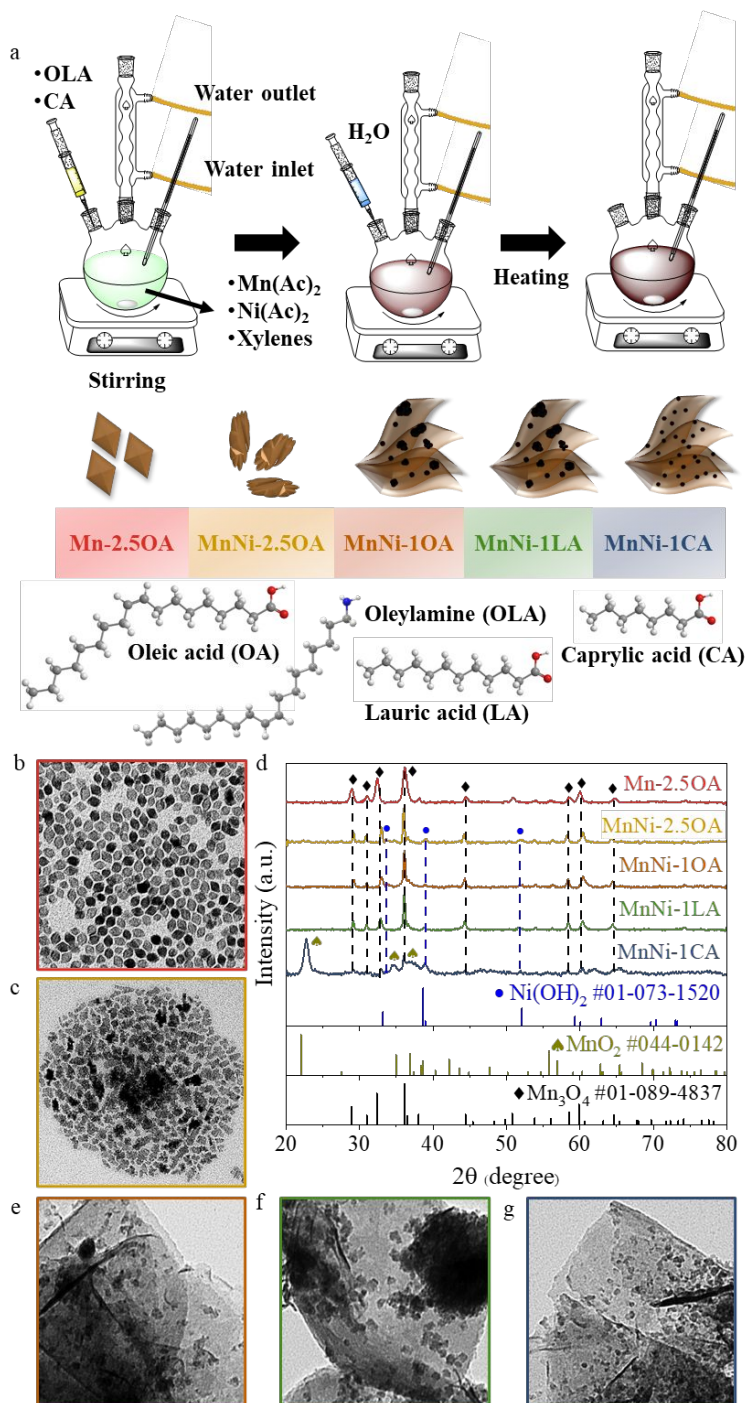
Mn_xO_y was synthesized through the decomposition of manganese acetate (MnAc₂) in the presence of OLA, OA and water in xylene at 100 °C and atmospheric conditions. The samples were labelled as Mn-2.5OA (manganese precursor with 2.5 mmol OA) and MnNi-2.5OA (same as Mn-2.5OA but with added nickel precursor). MnNi-1OA, MnNi-1LA, and MnNi-1CA were synthesized with both manganese and nickel precursors, where the carboxylic acid quantity was reduced to 1 mmol using OA, LA, and CA, respectively. TEM of Figure 1a reveals that the synthesized Mn_xO_y particles exhibit a bipyramidal morphology. XRD analysis further confirms that the Mn_xO_y particles primarily crystallize in the Mn₃O₄ hausmannite phase (Figure 1c).

When a 50 % molar mass (Ni vs. Mn) of nickel acetate (NiAc₂) was added to the reaction flask, irregularly shaped particles were obtained (Figure 1b). In addition to the Mn₃O₄ hausmannite phase, XRD patterns revealed diffraction peaks corresponding to the (100), (002), and (012) crystallographic planes of Ni(OH)₂ (Figure 1c, yellow line).

To assess the impact of OA on the growth of Mn_xO_y@Ni(OH)₂, both its concentration and carbon chain length were systematically varied. Reducing the OA concentration from 2.5 mmol to 1 mmol resulted in the formation of Mn_xO_y@Ni(OH)₂ self-supported nanoheterostructures where nanoparticles are supported on a nanosheet (Figure 1d). A similar morphology was observed when OA was replaced with 1 mmol of LA and CA (Figures 1e and 1f). Among these, the CA-derived sample exhibited the most homogeneous particle dispersion with minimal aggregation, suggesting a better stabilization effect.

XRD analysis confirmed that samples synthesized using OA and LA primarily contained Mn₃O₄ hausmannite and Ni(OH)₂ phases (Figure 1c). In contrast, the sample obtained with CA exhibited additional diffraction peaks corresponding to the (101), (301), and (210) crystallographic planes of the ramsdellite MnO₂ phase (Figure 1c), indicating a distinct structural evolution influenced by the carboxylic acid ligand.

1 The Mn and Ni content was quantified using ICP-OES analysis, with the results presented in Table
 2 S1. Overall, the Mn/Ni ratio remained consistent across all samples, closely matching the nominal
 3 values of the precursor materials, indicating reliable compositional control during synthesis.



4
 5 **Figure 1.** a) Schematic representation of the experimental procedure used to prepare the different
 6 samples, b) TEM micrograph of Mn-2.5OA and c) MnNi-2.5OA nanoparticles. d) XRD peaks of

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3 1 Mn-2.5OA, MnNi-2.5OA, MnNi-1OA, MnNi-1LA and MnNi-1CA. e-g) TEM micrograph of e)
4 2 MnNi-1OA, f) MnNi-1LA and g) MnNi-1CA.
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7 3 The structural and compositional analysis of the synthesized nanocomposites, demonstrated by
8 4 HRTEM images and HAADF-STEM with EELS, provides valuable insights into the phase
9 5 evolution and morphology of the samples. Figure 2 presents a detailed structural and compositional
10 6 analysis of $Mn_xO_y@Ni(OH)_2$ self-supported nanoheterostructures synthesized with varying
11 7 concentrations and chain lengths of carboxylic acids, specifically focusing on MnNi-2.5OA,
12 8 MnNi-1OA, and MnNi-1CA samples. HRTEM images (Figures 2a–c) reveal clear lattice fringes
13 9 for all three samples, with an interplanar spacing of $\sim 0.269\text{--}0.270$ nm indexed to the (100) planes
14 10 of $Ni(OH)_2$. These fringes confirm the crystalline nature of the $Ni(OH)_2$ component across all
15 11 samples.
16
17 12 The MnNi-2.5OA sample (Figure 2a) synthesized with a higher OA concentration demonstrates
18 13 well-defined and continuous lattice fringes, indicative of high crystallinity and structural integrity.
19 14 In contrast, reducing the OA concentration to 1 mmol (MnNi-1OA, Figure 2b) results in more
20 15 disordered nanosheet structures with embedded Mn_xO_y -supported nanoparticles. The lattice
21 16 fringes remain visible but slightly less distinct, suggesting a moderate impact on crystalline
22 17 ordering. ^[53-55] Interestingly, the MnNi-1CA sample (Figure 2c), derived using 1 mmol of CA—a
23 18 shorter-chain fatty acid—exhibits similarly ordered fringes but with improved overall
24 19 homogeneity and minimal visible aggregation.
25
26 20 The STEM-EELS mapping (Figures 2d–f) further underscores the influence of surfactant identity
27 21 on elemental distribution. In the MnNi-2.5OA sample, Ni, Mn, and O are uniformly distributed,
28 22 corresponding to well-stabilized and discrete nanoparticle assemblies. In contrast, the MnNi-1OA
29 23 sample shows clear nanoparticle aggregation, evident from the white contrast regions in the
30 24 HAADF-STEM image and overlapping Ni and Mn signals. This is attributed to the lower OA
31 25 concentration, which reduces steric stabilization during synthesis. Interestingly, the MnNi-1CA
32 26 sample exhibits a highly uniform elemental distribution with no obvious aggregation, despite CA's
33 27 shorter alkyl chain. This improved stabilization is likely due to CA's combination of steric and
34 28 electrostatic effects, which enhance particle dispersion at lower concentrations. ^[56-58] In summary,
35 29 these results highlight how both the concentration and molecular structure of carboxylic acid
36 30 surfactants critically influence the crystallinity, elemental distribution, and aggregation behavior

of the $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ nanoheterostructures. Lower OA concentrations lead to aggregation, while CA enables uniform particle dispersion even at reduced surfactant levels, demonstrating a clear correlation between synthesis conditions, structure, and composition.

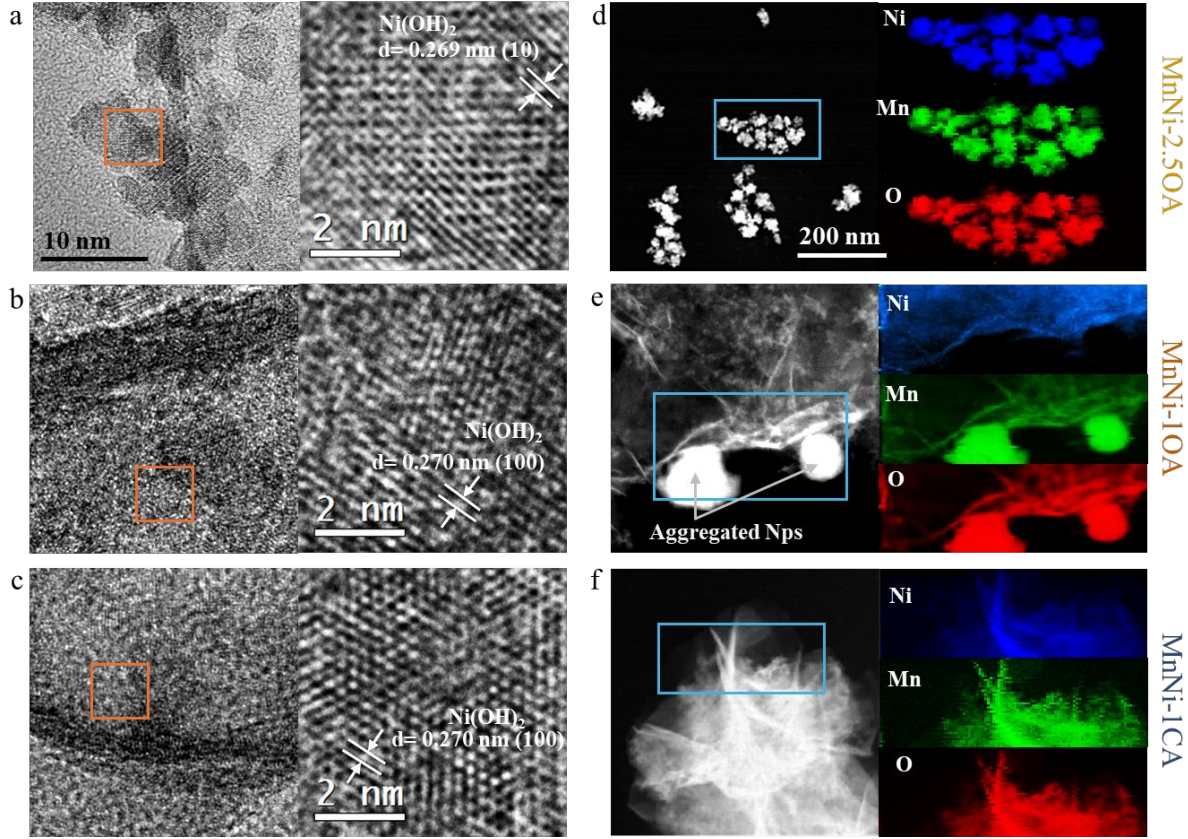


Figure 2. a-c) HRTEM micrographs with magnified lattice fringe visualized in the orange square and d-f) HAADF STEM general views of the nanostructures together with selected area STEM-EELS composition maps of the MnNi-2.5OA, MnNi-1OA and MnNi-1CA samples.

Figure 3 displays additional HRTEM images of the $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ nanoheterostructures obtained with CA. The nanosheet exhibits the crystal structure of $\text{Ni}(\text{OH})_2$ (Figure 3a), while the nanoparticles show the Mn_3O_4 and MnO_2 phases. The $\text{Ni } 2p_{3/2}$ XPS spectrum of $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ obtained with CA was deconvoluted into three peaks associated with Ni^{2+} in $\text{Ni}(\text{OH})_2$ at 853.6 eV, Ni^{3+} in NiOOH at 858.1 eV, and a satellite peak (Figure 3e). The $\text{Mn } 2p$ XPS spectrum displays two doublets corresponding to Mn^{3+} and Mn^{4+} oxidation states. These species, identified in the XPS spectra, are consistent with the Mn_3O_4 and MnO_2 phases observed in the HRTEM images, supporting the coexistence of both phases in the nanoheterostructures.

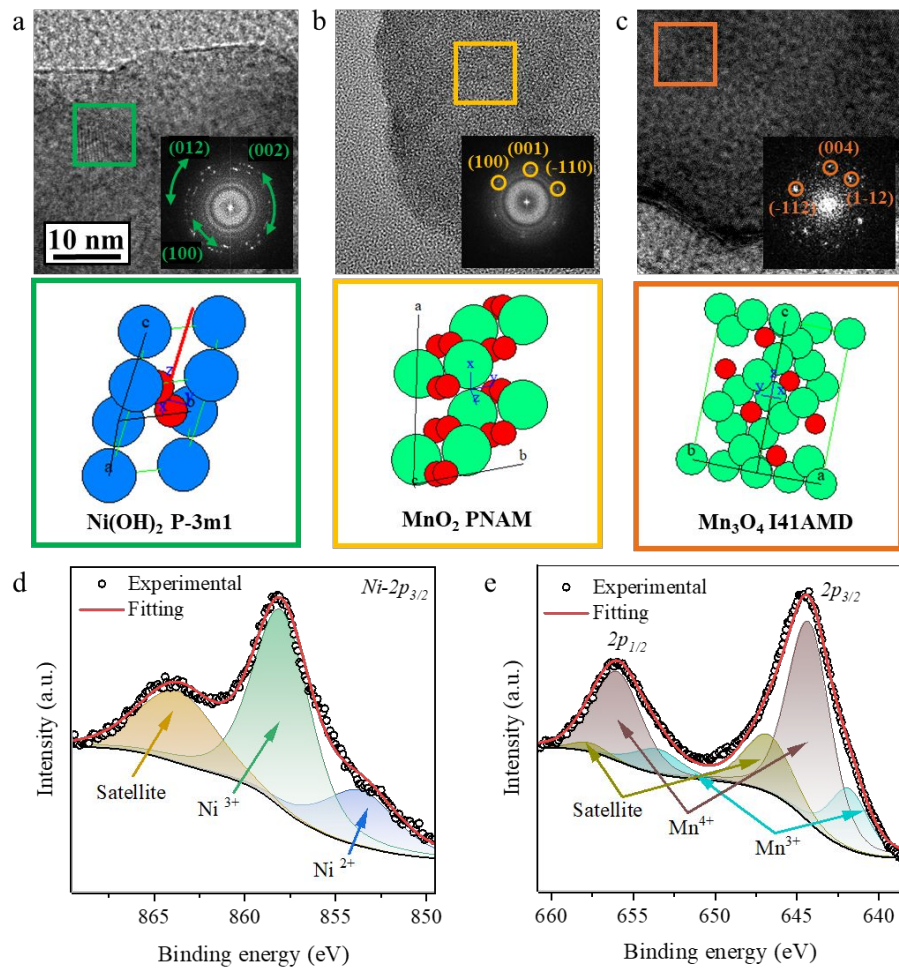


Figure 3. a-c) HRTEM micrographs, corresponding fast Fourier transformation (FFT) pattern (inset), and crystallographic structure models identified in each region of the MnNi-1CA sample. d, e) High-resolution Ni 2p_{3/2} and Mn 2p XPS spectra of MnNi-1CA.

The TEM micrographs and corresponding selected area electron diffraction (SAED) patterns of MnNi-1CA at different synthesis times reveal a time-dependent crystallization mechanism (Figure 4). After the addition of water, thin, sheet-like structures corresponding to Ni(OH)₂ begin to nucleate after 10 min of reaction, as confirmed by the diffraction rings of the (100) and (111) planes (Figure 4a). Water plays a critical role in the nucleation and growth of Ni(OH)₂, facilitating the hydrolysis and precipitation processes.^[7] As the reaction progresses, these nanosheets grow larger and more defined, with the appearance of the (112) plane indicating increased crystallinity and structural organization (t = 30 min, Figure 4b). By 60 min, the TEM image shows denser nanosheets with small nanocrystals forming on the surface, marking the transition from a pure hydroxide phase to a mixed-phase system, which is further validated by new SAED diffraction

1 rings corresponding to MnO_2 (303) and Mn_3O_4 (224), suggesting the progressive incorporation of
 2 Mn species. Finally, at 180 min, the morphology becomes more compact and granular, indicating
 3 the final stabilization of mixed metal oxides, with the SAED pattern exhibiting stronger MnO_2 and
 4 Mn_3O_4 reflections, including the (213) and (215) planes. This demonstrates the complete structural
 5 transformation from hydroxides to a stable mixed-metal oxide phase driven by prolonged reaction
 6 time, crystallization processes, and the presence of water.

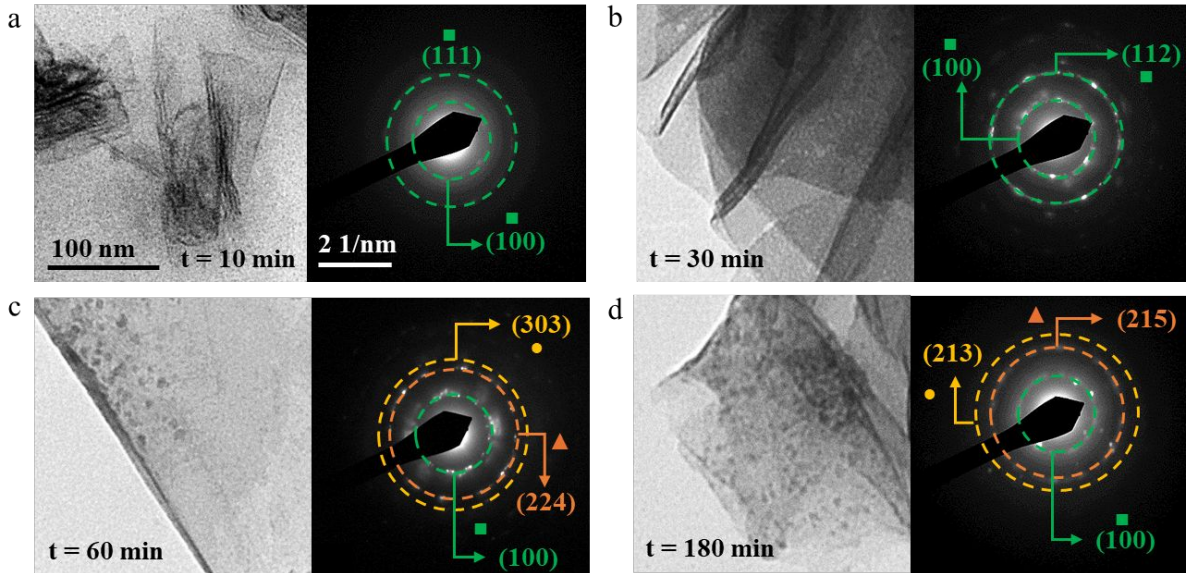


Figure 4. TEM micrograph and corresponding SAED pattern evolution of MnNi-1CA at different synthesis times: a) $t = 10$ min, b) 30 min, c) 60 min, and d) 180 min after water injection. The diffraction rings highlighted in green (■) correspond to the crystal structure of $\text{Ni}(\text{OH})_2$, while those in yellow (●) and orange (▲) are associated with the crystal structures of MnO_2 and Mn_3O_4 , respectively.

In addition to the critical role of water, the concentration of carboxylic acid ligands also significantly influences the crystallization pathway and final morphology. Experimental results using OA, LA and CA consistently show that lower ligand concentrations favor the formation of thin, two-dimensional heterostructures, whereas higher concentrations tend to stabilize smaller, more isotropic nanoparticles. This behavior is attributed to the dynamic competition between ligand adsorption and precursor nucleation: at low concentrations, partial surface coverage by carboxylate groups facilitates lateral growth of $\text{Ni}(\text{OH})_2$ nanosheets and the subsequent anchoring of Mn-based nanocrystals.

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3 1 DFT calculations using OA as a model ligand support this interpretation. The results reveal
4 2 preferential adsorption on the $\text{Mn}_3\text{O}_4\text{--MnO}_2$ region (-1.32 eV) of the $\text{Ni}(\text{OH})_2/\text{Mn}_3\text{O}_4\text{--MnO}_2$
5 3 heterostructure, compared to weaker adsorption on the $\text{Ni}(\text{OH})_2$ region (-0.94 eV), as shown in
6 4 Figure S5. This disparity suggests that ligand binding helps stabilize specific regions of the
7 5 heterostructure, promoting anisotropic growth and interface formation. The adsorption occurs
8 6 primarily via O and OH coordination from the carboxylic headgroup, a mode likely shared across
9 7 all three acids studied. These findings indicate that ligand concentration is the dominant factor in
10 8 directing 2D heterostructure assembly, with molecular identity playing a secondary role due to the
11 9 shared binding motif of carboxylic acids. However, the molecular structure of the ligand becomes
12 10 increasingly important in determining crystallinity, elemental distribution, and aggregation
13 11 behavior, as observed in the different outcomes for OA, LA, and CA at comparable concentrations.

12 **2.9. Electrochemical characterization**

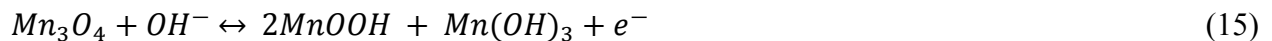
13 Electrodes were prepared by spray coating CC with a solution containing the $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$
14 and MWCNT. The combination of CC providing a conductive support, while MWCNT promote
15 the dispersion of active materials, results in efficient charge transfer, enhanced material
16 distribution, and improved electrochemical performance. SEM-EDS analysis (Figure S1-S4)
17 revealed a homogeneous coverage of the CC fibers. The LSV data have been iR-corrected and
18 normalized to the ECSA to allow for accurate comparison of intrinsic activity.^[59–62] Figure 5a
19 shows the curves in an alkaline electrolyte obtained for the different electrodes. ^[17] MnNi-1CA
20 exhibited the lowest η_{OER} (299 mV at 10 mA cm^{-2}) involving improved thermodynamics and the
21 lowest Tafel slope ($\beta=61$ mV dec^{-1} , Figure 5b), indicating superior OER kinetics.

22 Electrochemical impedance spectroscopy (EIS) was conducted to determine the charge transfer
23 resistance of each sample under kinetic control during the OER process. The experimental data
24 were fitted using an equivalent circuit consisting of a resistance (R1) in series with an
25 resistive/capacitive element (R2/CPE1) element, where R1 represents the solution resistance,
26 CPE1 accounts for the pseudocapacitance of the double layer, and R2 corresponds to the charge
27 transfer resistance (R_{ct}). MnNi-1CA exhibited the smallest semicircle in the Nyquist plot,
28 indicating the lowest R_{ct} value (9 Ω), as shown in Figure 5c. In addition, Figure 5d and Table S2
29 illustrate the correlation between η_{OER} , β , and R_{ct} across the different samples. These results
30 suggest that lower charge transfer resistance is associated with enhanced OER kinetics and

improved electrocatalytic activity. In particular, the superior performance of MnNi-1CA can be attributed to its more efficient charge transfer at the electrode–electrolyte interface, which facilitates faster reaction kinetics during the OER process.

The ECSA was determined by analyzing the double-layer capacitance (C_{dl}), acquired through CV at varying scan rates (Figures 5e and S6). Consistent with previous results, MnNi-1CA also demonstrated the highest ECSA value, at 0.25 cm² (Figure 5f and Table S3).

Figure 5g presents CV plots at 10 mV s⁻¹ for MnNi-2.5OA, MnNi-1OA, MnNi-1LA, and MnNi-1CA electrodes. In this figure, peak A₁ corresponds to the oxidation process of Ni(OH)₂, while A₂ represents the subsequent reduction of NiOOH. Peaks B₁ and B₂ reflect the overlapping oxidation and reduction processes of MnO₂ and Mn₃O₄. The peak current densities A₁/A₂ observed at lower potentials (~1.2–1.3 V vs. RHE) are consistent with the redox activity of Ni-based species (Equation 14). In contrast, the B₁/B₂ peaks, occurring at slightly higher potentials (~1.3–1.4 V vs. RHE), correspond to Mn-based redox reactions, including the formation of higher oxidation states such as MnOOH (Equation 15 and 16).^[63–65] The generation of oxyhydroxide species (*OOH) during these oxidation processes is essential for creating active sites that significantly enhance the overall OER (Equation 17). As demonstrated in equations 13–17, the oxidation of Ni(OH)₂, MnO₂, and Mn₃O₄ leads to the formation of *OOH species, which play a critical role in initiating and promoting the OER.^[45,66–68]



Among the tested samples, MnNi-1CA exhibited the highest peak current density at A₁ (Figure 5h), indicating the most efficient redox activity of the Ni(OH)₂/NiOOH couple. In contrast, the other samples demonstrated greater activity for the Mn₃O₄ and MnO₂ redox reaction (B₁), as evidenced by their higher current density peak values compared to that of the Ni(OH)₂/NiOOH redox peaks, but showed intrinsically lower activity than the Ni(OH)₂/NiOOH couple in the context of the OER. This observation suggests that MnNi-1CA possesses a greater number of

1 electrochemically active sites and enhanced charge transfer kinetics. Importantly, the overlapping
2 redox processes of Ni and Mn species create a dynamic interfacial environment where
3 simultaneous oxidation and reduction reactions facilitate efficient electron transfer and stabilize
4 critical *OOH intermediates. This synergistic overlap enhances the overall OER performance by
5 optimizing the availability and activity of catalytic sites on the electrode surface.

6 The superior performance of MnNi-1CA is attributed to the unique composition, where the
7 Ni(OH)₂ nanosheet supports both Mn₃O₄ and MnO₂ nanoparticles, in contrast to the other samples,
8 which only feature Mn₃O₄ nanoparticles on Ni(OH)₂ nanosheets. The presence of MnO₂ in MnNi-
9 1CA plays a crucial role in boosting catalytic performance, as it is more active for OER compared
10 to Mn₃O₄. Although Mn₃O₄ is less active for OER, it serves as both a precursor to MnO₂ under
11 OER conditions and as a stabilizing phase.^[69] Furthermore, the proton diffusion barrier, often a
12 rate-limiting factor in the Ni(OH)₂/NiOOH transition, is effectively reduced in MnNi-1CA. ^[70]
13 This is demonstrated by its highest surface coverage (Γ^*) and diffusion coefficient (D, Figures S5,
14 S7 and S8).

15 Complementary XPS analysis (Figure S9, Table S4) further supports this behavior, showing that
16 the Ni species remain in a stable NiOOH-like state after CV cycling, while Mn species undergo
17 redox evolution ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+}/\text{Mn}^{2+}$). This indicates that Mn₃O₄ serves as a redox-active yet
18 structurally stable support, promoting the activity of the NiOOH phase through dynamic surface
19 interactions.

20 When comparing the performance of sample MnNi-1CA (299 mV at 10 mA·cm⁻²) with current
21 state-of-the-art catalysts, a significant improvement in the overpotential is observed (Table S5).
22 For instance, the overpotential is clearly lower than those reported for Ni(OH)₂ MnO₂, and Mn₃O₄
23 (391, 381 and 370 mV, respectively), ^[34,40,71] and even compared to nanoheterostructures
24 containing MnO₂ combined with Ni or Ni(OH)₂ (580, 474, 410 and 400 mV, respectively).^[36-39]
25 Notably, the overpotential of MnNi-1CA also outperforms that of the benchmark OER
26 electrocatalyst RuO₂ (360 mV).^[35] Our results are only surpassed by recently developed atomically
27 dispersed Gd-MnO₂ nanoparticles and comparable to Gd@MnO₂ nanoheterostructures (281 and
28 323 mV, respectively). ^[71] This enhanced electrocatalytic performance can be attributed to the
29 synergistic interaction between Mn and Ni domains, as well as the formation of heterojunctions

within the nanoheterostructures —specifically between MnO_2 – Mn_3O_4 and these manganese oxides with the $\text{Ni}(\text{OH})_2$ nanosheet.

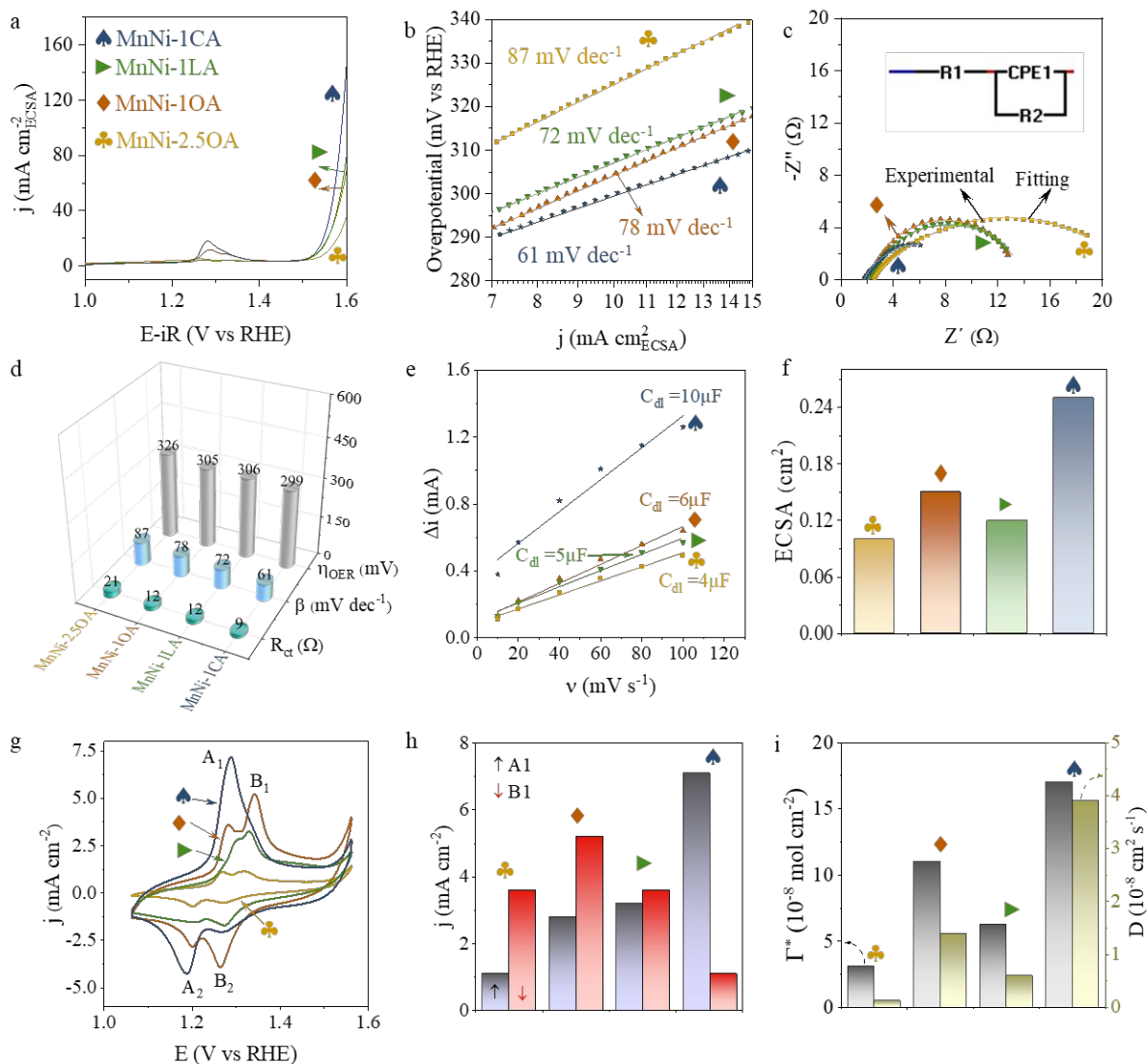


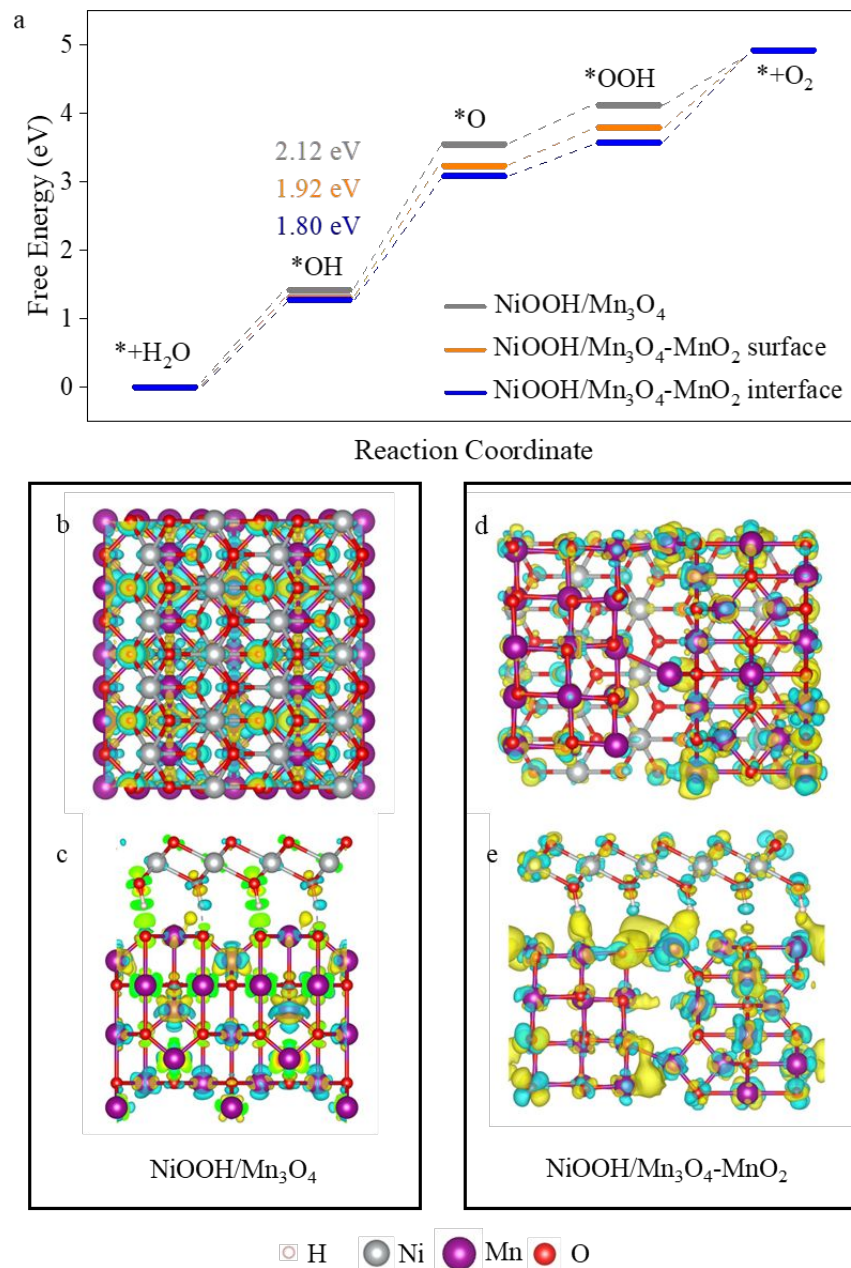
Figure 5. Electrochemical performance in 1 M KOH solution: a) LSV curves at 5 mV/s, b) Tafel plots, with the β extracted from the LVS curve at a $\eta_{\text{OER}} \pm 20$ mV c) Nyquist plots measured at η_{OER} and equivalent circuit used to fit the data (see Table S2 in the SI). d) Comparison of η_{OER} , β and R_{ct} . e) Determination of C_{dl} from the slope of the linear fit of Δi vs. v and f) ECSA. g) CV curve at 10 mV s⁻¹ and h) peak current densities extracted from CV curves at 10 mV s⁻¹, corresponding to the oxidation of $\text{Ni}(\text{OH})_2$ (A₁) and Mn_xO_y (B₁). i) Comparison of Γ^* and D of redox species for MnNi-2.5OA, MnNi-1OA, MnNi-1LA and MnNi-1CA.

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The stability of the MnNi-1CA sample was assessed through chronoamperometry at two different potentials. At a fixed potential of 1.7 V vs. RHE, which is above the OER overpotential, the current rapidly decreased within the first few hours, indicating significant electrode degradation under these harsher conditions (Figure S10a). In contrast, at a lower potential of 1.6 V vs. RHE, close to the onset potential, the material exhibited stable performance for about 24 hours. This suggests that MnNi-1CA is more durable under milder conditions, maintaining its activity over a longer duration without significant degradation. Moreover, LSV measurements taken before and after chronoamperometry at 1.6 V vs. RHE (Figure S10b) showed no significant change in current density across the tested potential window, further confirming that the material does not undergo noticeable degradation under these conditions. This stability at 1.6 V contrasts with its instability at higher potential values, indicating that MnNi-1CA is stable under milder operational conditions, but further optimization is required to improve its performance and stability at higher potential values for prolonged use.

In addition to experimental investigations, DFT calculations were performed to gain a fundamental understanding of the effect of single Mn_3O_4 and $\text{Mn}_3\text{O}_4\text{-MnO}_2$ heterostructure on the NiOOH OER performance. Considering only the four-electron ($4e^-$) reaction pathway shown in equations 7–10, the Gibbs free energy of each elementary step for the adsorbate evolution mechanism (AEM) either on the surface of NiOOH / Mn_3O_4 or NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ was calculated, respectively. The calculated adsorption structures are shown in Figures S11-S13. According to the calculations for the Gibbs free energy, the reaction of step II, from $\ast\text{OH}$ to $\ast\text{O}$, is the rate-determining step for both NiOOH / Mn_3O_4 (2.12 eV) and NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ (1.92 eV) with the overpotential of 0.89 V and 0.69 V, respectively (Figure 6a). Furthermore, the overpotential for the lattice oxygen oxidation mechanism (LOM) proceeded on the interface of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ is only 0.57 V. In this case, the largest Gibbs free energy change is 0.12 eV smaller than that for AEM on the surface of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$. Thus, the LOM mechanism requires a lower overpotential to drive the oxidation of water. Overall, our calculations show that the OER catalytic activity of NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$ can be significantly increased by introducing $\text{Mn}_3\text{O}_4\text{-MnO}_2$ heterostructure composite and that the LOM mechanism is more favorable, which is consistent with the experimental results. Furthermore, charge density differences were further analyzed comparatively for NiOOH / Mn_3O_4 and NiOOH/ $\text{Mn}_3\text{O}_4\text{-MnO}_2$. As shown in Figure 6, when $\text{Mn}_3\text{O}_4\text{-MnO}_2$ heterostructure served as the support for NiOOH, more electrons will transfer to the NiOOH and

1 accumulate especially on the interface of NiOOH/Mn₃O₄-MnO₂, leading to a convenient electron
 2 transfer from the catalysts to the oxygen species, which facilitates the OER through the electron
 3 modulation.



4
 5 **Figure 6.** a) Free energies of OER steps on the surface of NiOOH/Mn₃O₄ and surface/interface of
 6 NiOOH/Mn₃O₄-MnO₂. (b-e) Charge density difference of b) top-view and c) side-view of
 7 NiOOH/Mn₃O₄, d) top-view and e) side-view of NiOOH/Mn₃O₄-MnO₂. The isosurface is 0.002
 8 eÅ⁻³.

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1 Conclusion

$\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ was successfully synthesized using a low-temperature colloidal method. Notably, a reduction in carboxylic acid content from 2.5 to 1 mmol resulted in the formation of $\text{Ni}(\text{OH})_2$ nanosheets. This structural alteration proved pivotal in enhancing the electrochemical properties of the investigated materials for OER. Among the materials tested, MnNi-1CA exhibited the most promising outcomes, displaying a remarkably low overpotential of 299 mV at 10 mA cm⁻². This advantageous performance can be associated with its minimal Tafel slope (61 mV dec⁻¹), low R_{ct} value (9 Ω), and substantial surface-active area (0.53 cm²). These favorable characteristics can be attributed to the presence of a MnO_2 phase and in the formation of a Mn_3O_4 - MnO_2 heterostructure (heterojunction). Synergistic interactions among $\text{NiOOH}/\text{Mn}_3\text{O}_4$ - MnO_2 nanoheterostructures results in a catalytic environment that enhances charge transfer and stabilizes key oxygen evolution intermediates (*OH, *O, and *OOH). Moreover, DFT calculation along with experimental results points towards a LOM as the dominant OER mechanism delivering overpotential as low as 299 mV. Overall, this study provides new insights into the synthesis of $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ nanoheterostructures via the modulation of different ligands. This approach not only involves their evolution from 0D to a 2D arrangement but also highlights their enhanced electrochemical properties.

18 Supporting information

SEM images and EDS spectra of $\text{Mn}_x\text{O}_y@\text{Ni}(\text{OH})_2$ electrodes; DFT-calculated adsorption energies on NiOOH , Mn_3O_4 , and $\text{NiOOH}/\text{Mn}_3\text{O}_4$ - MnO_2 surfaces; CV curves and scan rate-dependent behavior; analysis of diffusion and kinetic parameters; post-CV XPS spectra of Mn and Ni; chronoamperometric stability tests and LSV curves before/after operation; optimized structures of OER intermediates (*OH, *O, *OOH) under AEM and LOM pathways; ICP-OES analysis of Mn/Ni ratios; thermodynamic, kinetic, and electrochemical parameters for OER; XPS quantification of surface states pre- and post-cycling; benchmarking of overpotential performance versus literature.

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