

Encapsulation of Ni nanoparticles in O-doped carbon as chainmail electrocatalyst for alkaline seawater hydrogen evolution

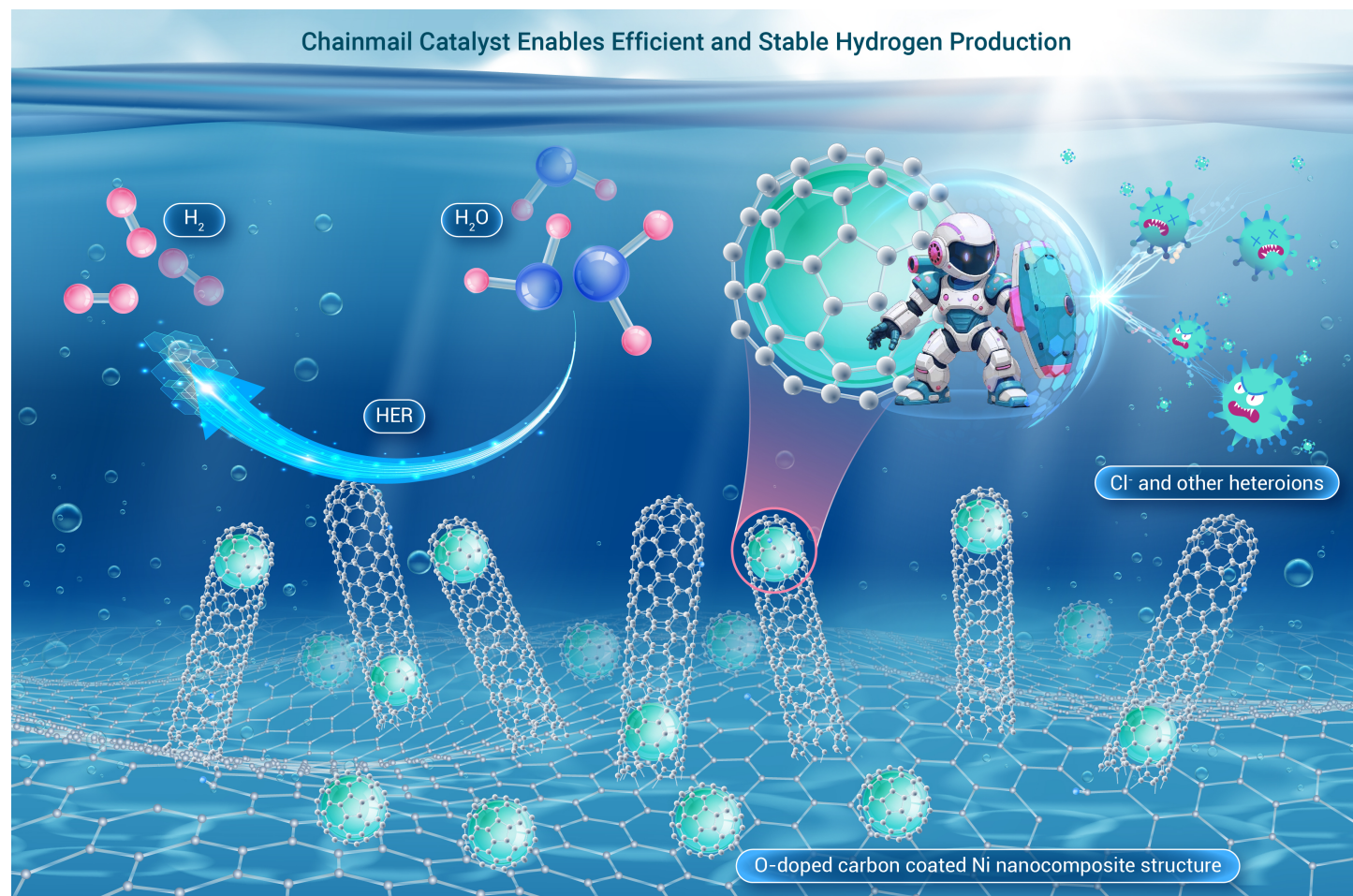
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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- A chainmail catalyst with O-doped carbon-coated Ni nanoparticles was made via salicylic acid intercalation.
- Ni@O-C/CNTs shows excellent hydrogen evolution reaction (58 mV) in alkaline seawater with >2000 h stability.
- In electrolyzer tests, Ni@O-C/CNTs achieves high efficiency and >300 h stability in real seawater.

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Carbon encapsulation represents a promising strategy for enhancing the activity and stability of the nanocatalysts *via* the chainmail approach, showing great potential in seawater electrolysis. Herein, a chainmail design is proposed to synthesize nickel nanoparticles protected with an O-doped graphitic shell on carbon nanotubes (Ni@O-C/CNTs) for highly efficient and stable hydrogen evolution reaction (HER) in alkaline seawater. Ni@O-C/CNTs are synthesized by *in situ* pyrolysis of salicylate intercalated layered nickel hydroxides, forming abundant Ni-O-C bonds at the interface. This chainmail design facilitates the penetration of valence electrons from the active Ni core to the graphitic shell, thereby promoting the adsorption of intermediates involved in HER. Moreover, the enriched O groups on CNTs enhance hydrophilicity and aerophobicity, facilitating electrolyte transport and hydrogen evolution during HER. Owing to the unique chainmail design, Ni@O-C/CNTs exhibit excellent HER performance in real alkaline seawater with a 58 mV overpotential at the current density of 10 mA cm⁻² and maintain stability at a current density of 150 mA cm⁻² over 2000 hours. Impressively, a high energy efficiency of 80% and stability of up to 300 hours are achieved for the alkaline seawater electrolyzer assembled using Ni@O-C/CNTs under practical conditions.

INTRODUCTION

Clean and renewable energy development has attracted widespread attention in addressing the dual challenges of the energy crisis and air pollution caused by fossil fuel utilization.¹⁻⁵ Green hydrogen, characterized by its high energy density, zero-carbon emission, and sustainability, holds great promise as a clean energy source. Electrocatalytic hydrogen evolution reaction (HER) offers a viable route for high-purity hydrogen generation.⁶⁻¹⁰ However, the scarcity of ultrapure water poses a challenge to green hydrogen production, making seawater an inexhaustible alternative due to its abundance.¹¹⁻¹⁶ Notably, seawater electro-splitting faces obstacles due to the high concentrations of Cl⁻, which results in corrosive hypochlorite and chlorine formation. These byproducts block active sites, reduce H₂ production efficiency, and induce electrode corrosion.¹⁷⁻¹⁹ In addition, insoluble residues (dust, colloids, and bacteria) present in seawater can also cause catalyst deactivation and reduced durability.²⁰⁻²² Therefore, designing catalysts that exhibit both excellent activity and satisfactory stability for seawater HER remains a significant challenge.

Recently, the concept of chainmail catalysts has been proposed as an effective strategy to enhance catalyst activity and stability by encapsulating transition metal active species within carbon shells.²³⁻²⁵ The unique core-shell structure facilitates rapid electron transfer to active species and protects the active species against degradation, enhancing catalytic performance.²⁶⁻²⁸ For example, Deng *et al.* successfully encapsulated CoNi nanoalloys with ultrathin graphene shells, which facilitated the adsorption of hydrogen atoms onto the graphene surface through enhanced electron penetration from the CoNi nanoalloys to the graphene, resulting in superior and stable HER activity.²⁶ The chainmail structure not only prevents the migration of reactive species but also protects them from direct attacks by corrosive or oxidative electrolytes.^{29,30} For instance, Yang and his coworkers developed a metal-organic framework (MOF)-derived CoMn-NCNTFs/NF (where NF stands for Ni foam)

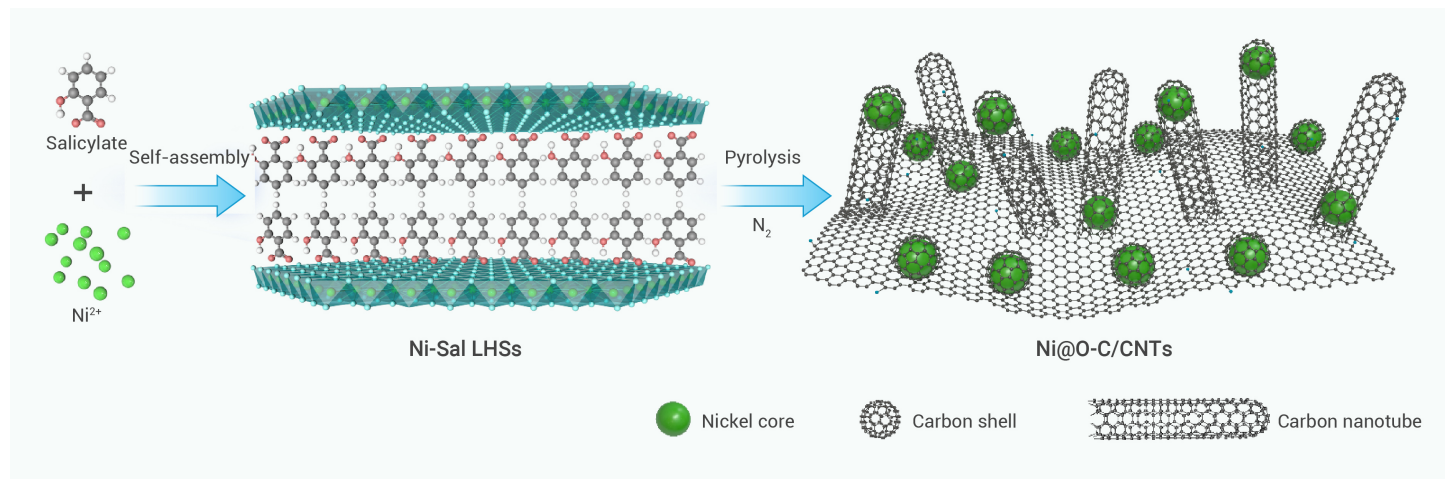
catalyst in which a metal-coated carbon layer not only acts as an anti-corrosion protective barrier for CoMn-NCNTFs/NF but also improves the material's electrical conductivity, thus ensuring its excellent HER activity and stability in true alkaline seawater.³⁰ Although the chainmail structure offers advantages in improving the reaction durability of metal catalysts under harsh conditions, so far, most reports have focused only on the exploitation of novel preparation methods and the precise regulation of composition. The effect of heteroatoms, particularly O-containing functional groups, on accelerating the HER activity of metal@C core-shell structures, has frequently been disregarded, despite the widespread acknowledgment of their significant impact on the reactivity of carbon materials.^{31,32} Layered hydroxide salts (LHS) [M²⁺(OH)_{2-x}(An)_{x/n}·mH₂O], as a novel type of layered materials with adjustable compositions and tunable intercalated organic anions, offer an ideal platform for the preparation of transition metal-carbon hybrid nanomaterials functionalized with specific groups.^{31,33,34}

Herein, we report a cost-effective direct pyrolysis method for synthesizing nickel nanoparticles encapsulated within O-doped carbon (Ni@O-C/CNTs) as chainmail electrocatalysts, by using an oxygen-rich organic molecule intercalated layered nickel hydroxide as the precursor. This approach leverages salicylic acid as a carbon source, enabling one-step synthesis of carbon nanotube arrays while minimizing material and processing costs. The pyrolysis process results in uniformly dispersed nickel nanoparticles that are encapsulated by graphitic carbon and intricately intertwined with *in situ*-grown carbon nanotubes catalyzed by nickel nanoparticles. Notably, the pyrolysis of salicylate intercalated layered nickel hydroxides leads to the formation of abundant Ni-O-C bonds at the interface, fostering a strong interaction between the nickel core and graphitic carbon shell. This unique carbon shell structure not only facilitates rapid electron transfer to active sites but also provides exceptional corrosion resistance, thereby endowing the material with excellent activity and long-term stability in harsh seawater environments. Furthermore, the dense network of carbon nanotubes significantly increases the material's mesoporosity and conductivity, thereby improving the contact with the electrolyte and enhancing mass transfer. Remarkably, Ni@O-C/CNTs exhibit excellent catalytic activity towards HER in various alkaline electrolytes, with low overpotentials of 33 mV, 47 mV, and 58 mV in 1 M KOH, 1 M KOH + simulated seawater, and 1 M KOH + real seawater, respectively, at a current density of 10 mA cm⁻². Moreover, excellent long-term durability and cyclic stability are observed for HER. When tested in actual alkaline seawater at a current density of 150 mA cm⁻², Ni@O-C/CNTs maintained excellent performance even after 2000 hours. Furthermore, when combined with commercial IrO₂ as catalysts in water/seawater electrolysis systems, the Ni@O-C/CNTs || IrO₂ pairs surpassed the benchmark Pt/C || IrO₂ pairs in overall performance. The ability of the Ni@O-C/CNTs to sustain stable electrolysis for up to 300 hours under true alkaline seawater conditions underscores their potential for sustainable and efficient hydrogen production through water/seawater electrolysis.

MATERIALS AND METHODS

Synthesis of Ni-Sal LHSs

Typically, an aqueous solution of sodium salicylate (0.04 mol) was added to a flask containing an aqueous solution NiCl₂·6H₂O (0.02 mol) with continu-



Scheme 1. Schematic illustration of the fabrication process of Ni@O-C/CNTs nanocomposite.

ous stirring in deionized water (250 mL) at 25°C. Then, NaOH solution (0.5 M) was introduced into the above homogeneous solution to maintain a pH of 8. The resultant solution was then heated at 95°C in an oil bath and kept stirring for 24 h. After the reaction, the mixture was cooled down to room temperature. The green precipitates were collected by centrifugation, then washed with deionized water several times, and finally dried at 40°C in air overnight.

Synthesis of Ni@O-C

For the preparation of Ni@O-C, the Ni-Sal LHSs were used as the precursor for annealing at 700°C for 2 h under a nitrogen flow with a heating rate of 5 °C·min⁻¹, and the total flow of gas is 45 mL·min⁻¹.

Electrochemical measurements

All the electrochemical measurements were performed in a standard three-electrode cell at room temperature using an electrochemical workstation (CHI660E), consisting of a modified glassy carbon working electrode (GCE, a diameter of 3 mm), an Ag/AgCl reference electrode, and a platinum (Pt) wire counter electrode. To prepare the Ni@O-C on the glassy carbon electrode, 5 mg catalyst was mixed with 120 µL 5wt% Nafion solution, 540 µL ethanol, and 340 µL deionized water by at least 30 min sonication to form a homogeneous ink. Subsequently, 4 µL suspension was drop-dried onto a glassy carbon electrode (loading of ~0.28 mg cm⁻²). The LSV curves were recorded at a scan rate of 5 mV s⁻¹ and were measured in 1 M KOH, 1 M KOH + 0.5 M NaCl, and 1 M KOH seawater, which were used as electrolytes. The seawater is taken from Qingdao, Shandong Province. All the potentials were converted to the potentials referring to the RHE (with *iR* correction), according to $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.059 \text{ pH} + 0.197$.

MEA measurements

The MEA setup with a geometric area of 1 cm² was purchased from Gaosunion. For anode and cathode samples, the catalyst ink is prepared as follows: 5 mg catalyst is ultrasonically dispersed in a 1000 µL solution containing 340 µL deionized water, 540 µL ethanol, and 120 µL 5 wt% Nafion. The cathode and anode materials were drop-coated onto nickel foam and separately assembled on both sides of the membrane to form a membrane electrode assembly (MEA). The catalyst loading for both the cathode and anode was 2 mg cm⁻². 1 M of hot KOH solution flowed through the MEA with a flow velocity of 20 mL min⁻¹. The temperature of MEA was measured as 60°C. The energy efficiencies discussed in this study pertain solely to the electrolysis cell. The theoretical voltage (E_0) for water splitting at 60°C was determined using the equation $E_0 = -(\Delta H - T\Delta S) / nF$, where ΔH is the enthalpy change for water splitting (-285.8 kJ mol⁻¹), T is the reaction temperature, ΔS is the entropy change for water splitting (-163.34 J K⁻¹ mol⁻¹), n is the number of electrons transferred ($n = 2$), and F is the Faraday constant (96485 C mol⁻¹). The energy efficiency of the electrolysis cell is defined as the ratio of the net energy stored in the hydrogen produced to the net energy consumed by the cell.³⁵ The energy stored in the hydrogen is represented by its higher heating value, which is 39.4 kWh kg⁻¹.

DFT calculations

All first-principles calculations were based on spin-polarized density func-

tional theory (DFT), using the DS-PAW (HZWTECH) software and employing the projector augmented wave (PAW) method.³⁶ Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional was used for the electron exchange-correlation function.³⁷ 4×4 supercells of (111) surface of Ni@C and Ni@O-C were constructed with a vacuum layer of 10 Å. During the structure optimization, the convergence of all models was set to less than 1.0×10⁻⁵ eV for energy and 0.02 eV Å⁻¹ for remaining forces. The plane wave cutoff was set with 500 eV and the Gamma k-point mesh was set to 3×3×1. The free energy of the adsorption intermediate state was calculated as $\Delta G = \Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T\Delta S$, where ΔE_{DFT} is the energy calculated by DS-PAW.

RESULTS AND DISCUSSION

Synthesis and characterization of Ni@O-C/CNTs

The Ni@O-C/CNTs nanocomposite was synthesized by using salicylate intercalated nickel hydroxides (Ni-Sal LHSs) as a precursor (Scheme 1). The process began with the preparation of Ni-Sal LHSs through the self-assembly of nickel ions with sodium salicylate under pH-controlled conditions. Sodium salicylate, an organic compound containing one hydroxyl group and one carboxyl group, played a crucial role in this step. Subsequently, the Ni-Sal LHSs precursor underwent pyrolysis at 700°C in an inert atmosphere, resulting in the decomposition and carbonization of the interlayer salicylate. Nickel cations were simultaneously reduced into metal nanoparticles, resulting in the formation of black Ni@O-C/CNTs nanocomposite. The microcrystalline structure of the products was first investigated using powder X-ray diffraction (XRD). The XRD pattern of Ni-Sal LHSs precursor exhibits a typical layered structure pattern with well-ordered (00 l) peaks, indicating the high purity and crystallinity of Ni-Sal LHSs (Figure 1A).³⁸ After pyrolysis, all the peaks could be attributed to metallic nickel (JCPDS #04-0850), indicating that the layered structure of the Ni-Sal LHSs was destroyed and the metal ions transformed into metallic form. No additional impurity was detected. The morphology evolution of the products was demonstrated using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Ni-Sal LHSs showed a typical two-dimensional stacked sheet-like morphology with an interplanar distance of ~1.23 nm (Figure S1), consistent with the XRD pattern. The representative SEM and TEM images of Ni@O-C/CNTs provide evidence for the formation of uniformly dispersed Ni nanoparticles, which are intricately intertwined with carbon nanotubes synthesized in situ (Figure 1B). These CNTs exhibit lengths ranging from 200 to 300 nm and diameters between 10 and 20 nm, prominently protruding from the carbon matrix. In addition, a large number of spherical nickel nanoparticles with an average size of 4~10 nm are observed to be encapsulated within the carbon shells consisting of several graphitic layers without severe agglomeration (Figure 1C). It is worth noting that a hybrid growth mechanism, involving both top- and bottom-growth of CNTs was observed, contingent on the size of Ni nanoparticles.³⁹⁻⁴¹ This unique structure is further confirmed by high-resolution TEM (HRTEM), showing a clear lattice fringe at the core with a d-spacing of 0.204 nm, corresponding to the (111) plane of the Ni nanoparticles (Figure 1D). The AC-HAADF-STEM characterization conclusively confirms the absence of isolated Ni single atoms (Figure S2). In addition, the Ni nanoparticles are distinctly surrounded by 2-3 layers of graphitic carbon shells at an

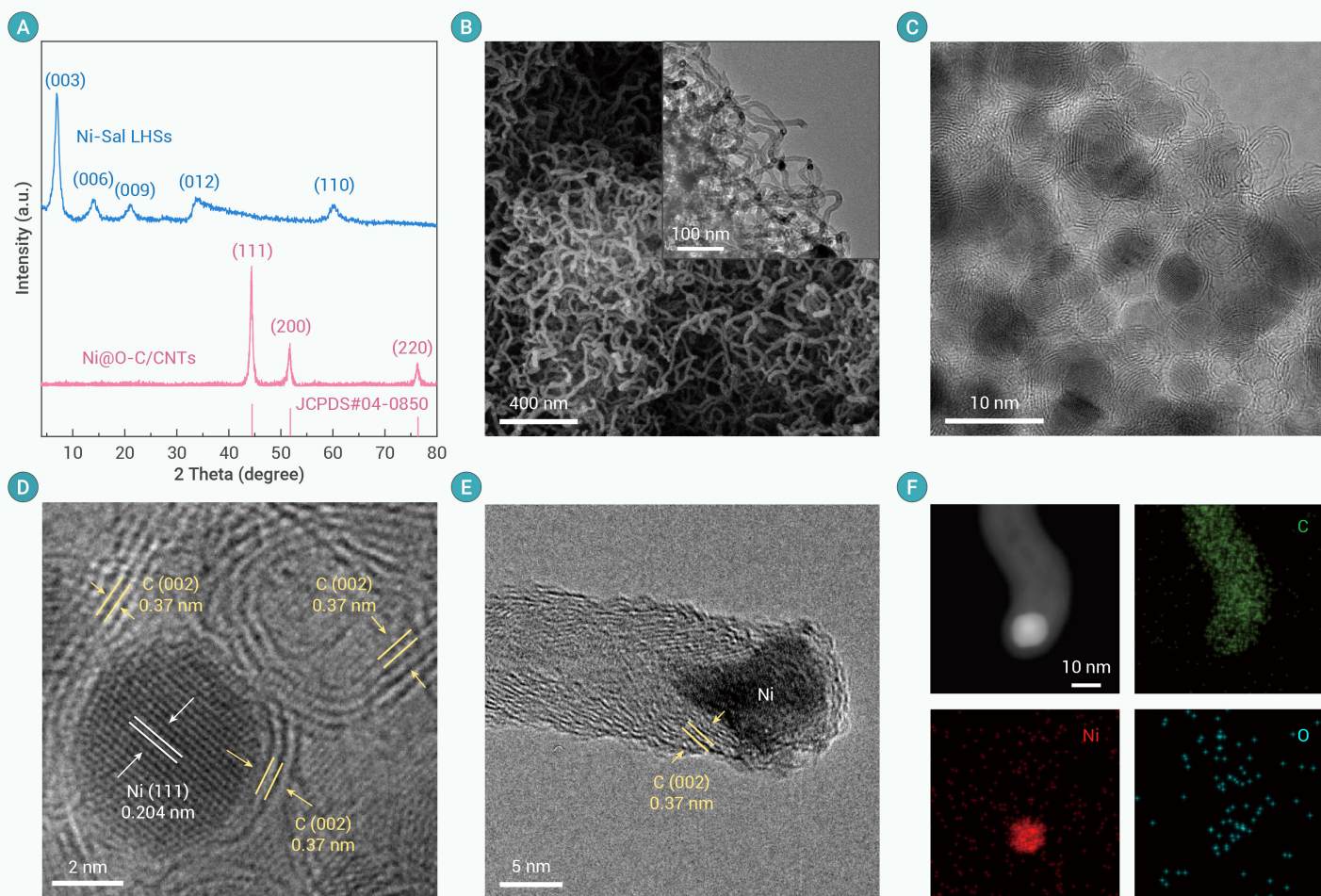


Figure 1. Structural characterization of Ni@O-C/CNTs catalyst (A) XRD patterns of Ni-Sal LHSs and Ni@O-C/CNTs. (B) SEM and TEM (inset of B), (C, D, E) HRTEM, and (F) HRTEM-EDS elemental mapping images of Ni@O-C/CNTs.

interlayer distance of about 0.37 nm, slightly larger than that of graphite ($d_{002} = 0.34$ nm), which may be attributed to the oxygen doping. These thin graphitic carbon shells provide effective protection for nickel nanoparticles against electrolyte corrosion and improve the stability and conductivity of the catalyst. Energy dispersive X-ray spectroscopy (EDX) mapping images further confirm the coexistence of Ni, O, and C in the Ni@O-C/CNTs (Figures 1F & S3). In addition, Ni-Sal LHS precursors were pyrolyzed at different temperatures for comparison, leading to the formation of Ni@O-C/CNTs-600 and Ni@O-C/CNTs-800. Figure S4 demonstrates that the growth of carbon nanotubes is impeded at lower temperature (600°C), resulting in a thicker carbon shell structure in the carbon-coated samples. Conversely, elevated temperature (800°C) induced the sintering of nickel nanoparticles and the formation of fragile carbon shells.⁴² Thus, an optimal pyrolysis temperature of 700°C was determined to facilitate the formation of unique structures with appropriate size of nickel nanoparticles and a moderate thickness of the outer carbon layer.

Further analysis of the chemical states of Ni@O-C/CNTs was conducted using X-ray photoelectron spectroscopy (XPS). In the high-resolution Ni 2p XPS spectra of Ni@O-C/CNTs (Figure 2A), the peak at 852.3 eV was attributed to the Ni 2p_{3/2} of metallic Ni, indicating that nickel ions in the precursor were successfully reduced in the pyrolysis process.³⁸ The peaks at 853.8 eV and 855.5 eV could be attributed to the presence of Ni-C and Ni-O-C bonds, indicating the strong interaction between Ni nanoparticles and graphitic carbon, which consequently results in a reduction of local electron density and higher binding energy at the Ni sites.⁴³ This interaction was also evidenced by the high-resolution C 1s spectrum of Ni@O-C/CNTs, which displayed two characteristic peaks for C-Ni at 283.6 eV and C-O-Ni at 288.5 eV (Figure 2B).⁴⁴ Notably, the C-O-Ni bonds are important for preventing the aggregation of metal nanoparticles and facilitating electron transfer between metal nanoparticles and graphitic carbon matrix during electro-

catalysis, thus enhancing the adsorption of intermediates involved in the electrochemical hydrogen evolution reaction process.⁴⁵ The peaks at 285.5 and 286.2 eV corresponding to carbon in C-O-C and C-OH, respectively, are attributed to the sp³-hybridization of graphite-like carbon.⁴⁶ The presence of hydrophilic C-OH groups in the catalyst facilitates the adsorption of water molecules through hydrogen bonding, thus improving the wettability of the catalyst and accelerating the water-splitting process.⁴⁷ Moreover, the high-resolution O 1s spectrum (Figure 2C), which can be deconvoluted into three peaks at 530 eV (Ni-O-C), 532 eV (C-OH), and 533.9 eV (H-OH),⁴⁸ further confirms the existence of abundant oxygen-containing functional groups originating from salicylate in the pyrolyzed product. Similar to Ni@O-C/CNTs, the presence of Ni-C and Ni-O-C is evident in the high-resolution Ni 2p and C 1s XPS spectra of both Ni@O-C/CNT-600 and Ni@O-C/CNT-800 (Figure S5). However, the O 1s spectra indicate that Ni@O-C/CNTs exhibited the highest peak of H-OH at 533.9 eV among all three samples, signifying their superior water adsorption capacity. The presence of a large number of oxygen-containing functional groups, particularly hydroxyl groups, in the Ni@O-C nanocomposites, was further identified using Fourier-transform infrared (FT-IR) spectroscopy (Figure 2D). This was evident from the broad bands observed at approximately 3441 cm⁻¹, attributing to the stretching vibrations of O-H, alongside a band at 1634 cm⁻¹ corresponding to the bending vibrations of O-H. Additionally, characteristic bands were identified at roughly 1264 cm⁻¹ and 1045 cm⁻¹ for C-O-C and C-OH stretching vibrations, respectively, in the FT-IR spectra. These abundant hydrophilic oxygen-containing functional groups in the catalyst greatly enhance the material's wettability in the electrolyte, as evidenced by the smallest contact angle (CA) of Ni@O-C/CNTs (25.2°) with a KOH (1 M) droplet among the three samples (Figure 2E), which could facilitate the liquid electrolyte transfer.⁴⁸ Simultaneously, the material exhibits superior gas-repellent properties, as evidenced by the gas contact angles of all three samples exceeding 90° (Figures 2E & S6). This

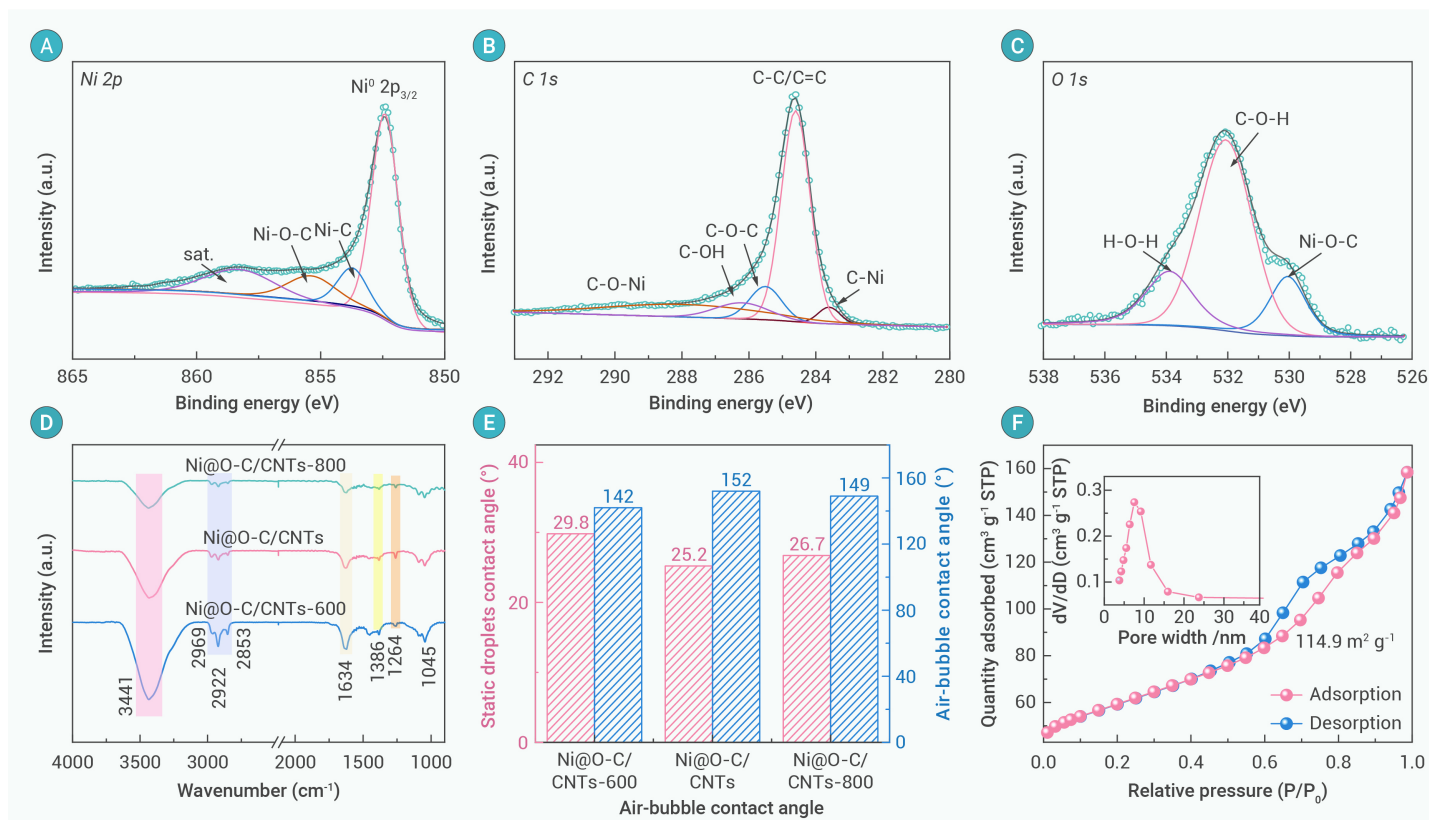


Figure 2. Compositional and surface characterization of Ni@O-C/CNTs (A–C) High-resolution XPS spectra of (A) Ni 2p, (B) C 1s and (C) O 1s of Ni@O-C/CNTs. (D) FT-IR spectra of the products after calcination of Ni-Sal LHSs at different temperatures. (E) The static droplets contact angles and the air-bubble contact angles of as-prepared products. (F) The N_2 adsorption/desorption isotherms and BJH pore size distributions (inset) of Ni@O-C/CNTs.

underscores the material's ability to effectively repel gaseous substances, further validating its potential applications in scenarios requiring gas-repellency.^{49,50} The Raman spectrum of Ni@O-C/CNTs exhibits two prominent bands corresponding to defective (D) and graphitic (G) carbons at 1320 cm^{-1} and 1596 cm^{-1} , respectively (Figure S7). The relative intensity ratio of the D band and G band (I_D/I_G) value of the Ni@O-C/CNTs is measured as 1.11 (Table S1), indicating the formation of a highly defective graphitic structure. This observation is consistent with the fact that the pyrolytically generated carbon material is rich in defect sites, which play a key role in inhibiting the aggregation of nanoparticles as well as improving the catalytic performance.^{51,52} The N_2 adsorption/desorption isotherms (Figure 2F) and the Barrett-Joyner-Halenda pore size distribution (inset Figure 2F) of Ni@O-C/CNTs exhibit similar type IV behaviors with an evident H3-type hysteresis loop ($P/P_0=0.4-0.9$), which indicates the mesoporous distribution characteristics in the catalyst. The Brunauer-Emmett-Teller (BET) specific surface area of Ni@O-C/CNTs is 114.9 $m^2 g^{-1}$, slightly larger than the other control samples (Figure S8, Table S2). The high specific surface area and uniform mesoporous structure of Ni@O-C/CNTs nanocomposites could be attributed to the entangled carbon nanotubes and uniformly dispersed nanoparticles. This structural feature provides more available reaction channels, facilitating the diffusion of electrolyte and product molecules, and thereby enhancing catalytic activity.

HER performance of Ni@O-C/CNTs in different electrolytes

HER performance of Ni@O-C/CNTs in alkaline water. The HER activity Ni@O-C/CNTs was evaluated in a standard three-electrode setup. Commercial Pt/C and samples with different pyrolysis temperatures were also compared. First, the HER activity of the samples was evaluated on the GC electrode in the electrolyte solution of pH=14 (1 M KOH), as shown in Figure 3A. As expected, Ni@O-C/CNTs exhibited excellent activity at a current density of 10 $mA cm^{-2}$, with an overpotential of 33 mV, which is smaller than that of Ni@O-C/CNTs-600 (92 mV), Ni@O-C/CNTs-800 (124 mV), and comparable to 20% Pt/C. Impressively, the HER activity of Ni@O-C/CNTs surpassed that of commercial 20% Pt/C when the current density exceeded 55 $mA cm^{-2}$. Furthermore, the catalytic kinetics of the electrode were evalu-

ated using the linear fit Tafel curve derived from the polarization data. As shown in Figure 3B, the Tafel slope of Ni@O-C/CNTs was 49 $mV dec^{-1}$, significantly lower than those of Ni@O-C/CNTs-600 (115 $mV dec^{-1}$) and Ni@O-C/CNTs-800 (136 $mV dec^{-1}$). This low overpotential and small Tafel slope of Ni@O-C/CNTs makes it one of the best HER catalysts under alkaline conditions compared with previously reported Ni-based HER electrocatalysts (Figure 3C, Table S3). Generally speaking, the Tafel slope can serve as a reference for inferring the rate-determining step (RDS) of HER.⁵³ According to the Tafel slope value of 49 $mV dec^{-1}$, the HER on the surface of the Ni@O-C/CNTs is likely based on the Volmer-Heyrovsky mechanism, indicating that the rate-determining step in the catalytic process is the dissociation of H_2O molecules. The small Tafel slope suggests that Ni@O-C/CNTs have a fast HER rate and a high water dissociation efficiency.

The electrochemical double-layer capacitance (Cdl) of the catalysts was further evaluated by cyclic voltammetry (CV) to estimate the electrochemical surface area (ECSA) of the catalyst (Figure S9).⁵⁴ The Cdl value of the Ni@O-C/CNTs with the best performance was 19.15 $mF cm^{-2}$, higher than those of other samples (Figure 3D). The calculated ECSA of Ni@O-C/CNTs was determined to be 478.8 cm^2 , higher than those of the samples (Table S4). Importantly, the specific HER activity of Ni@O-C/CNTs (normalized by ECSA) was significantly superior to other samples (Figure S10), suggesting that the increased activity stemmed from an intrinsic activity enhancement. In addition, the charge transfer resistance (Rct) of the four catalysts was analyzed by electrochemical impedance spectroscopy (EIS) measurements (Figure 3E). The lowest Rct of Ni@O-C/CNTs indicates the fastest electron transfer at the interface between metallic Ni and the thin graphite carbon shell.⁵⁵ These results confirm that the abundant and effective interface characteristics play a crucial role in enabling rapid electron transfer and active sites, which are key for enhancing the HER performance. Besides activity, electrocatalyst durability is equally critical for practical applications. Both time-dependent current density curves (Figure 3F) and the LSV curves after 1000 CV cycles (Figure 3F inset) reveal that Ni@O-C/CNTs electrode exhibited good long-test durability with negligible current loss after cycling for 1400 h and 1000 cycles. It is worth mentioning that the Ni@O-C/CNTs showed no obvious changes in either morphology or crystal structure after the durability tests (Figure S11),

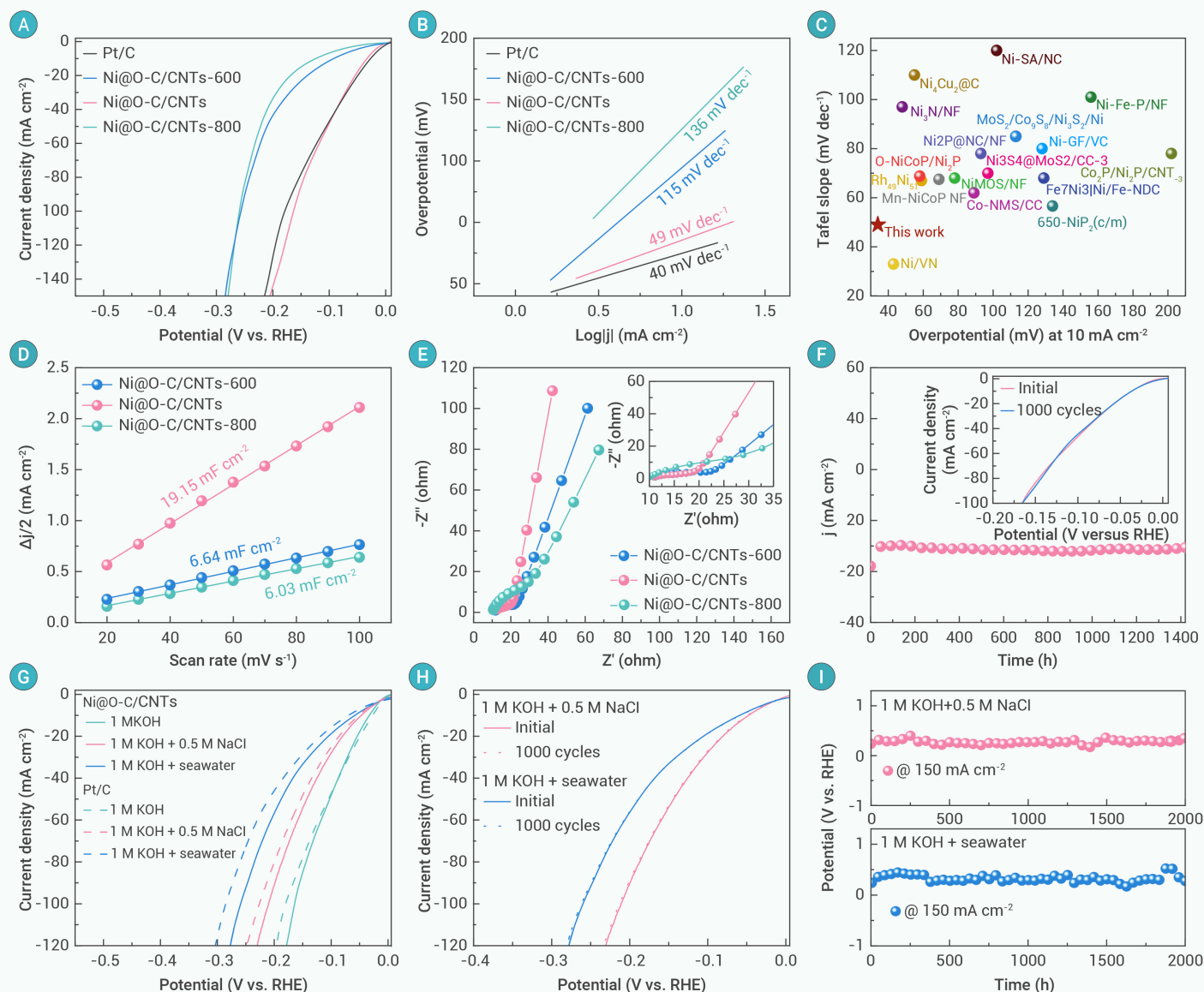


Figure 3. Electrocatalytic HER performance of Ni@O-C/CNTs (A, B) LSV curves (A) and Tafel plots (B) of Ni@O-C/CNTs and reference samples in 1 M KOH with a scan rate of 5 mV s⁻¹. (C) Comparison of overpotentials and Tafel slopes of Ni@O-C/CNT at a current density of 10 mA cm⁻² with other state-of-the-art catalysts. (D, E) The C_{dl} (D) and Nyquist plots (E) of as-prepared samples. (F) The time-dependent current density curve of Ni@O-C/CNTs for 1450 h. Inset: LSV curves for Ni@O-C/CNTs before and after 1000 CV cycles. (G-H) Comparative HER performance of Ni@O-C/CNTs between alkaline water, simulated alkaline seawater, and real alkaline seawater electrolytes: (G) LSV curves with a scan rate of 5 mV s⁻¹. (H) LSV curves before and after CV cycling. (I) Stability tests of Ni@O-C/CNTs at the current density of 150 mA cm⁻².

indicating the good structural and electrocatalytic stability of the Ni@O-C/CNTs. It is well known that the SCN⁻ complexation with metals can deactivate the catalytic sites.⁵⁶ The LSV curves of Ni@O-C/CNTs in 1 M KOH solution were compared before and after the addition of 10 mM SCN⁻ ions (Figure S12). Only a slight decrease in current density was observed upon the addition of SCN⁻, highlighting the effectiveness of thin graphitic carbon layers in Ni@O-C/CNTs, which make the Ni sites less susceptible to attack from nucleophilic reagents.

HER performance of Ni@O-C/CNTs in alkaline seawater. Utilizing the most abundant seawater resources on earth as the source of electrolytic water without additional treatment can alleviate the tension of water resources. Hence, it is crucial to develop an electrocatalyst suitable for seawater splitting so that H₂ can be produced on a large scale to meet the increasing energy demand.⁵⁷ We further study the electrochemical HER properties of Ni@O-C/CNTs in simulated alkaline seawater and real alkaline seawater solution. It can be observed from Figure 3G that the Ni@O-C/CNTs catalyst exhibits a lower overpotential at 10 mA cm⁻² in simulated alkaline seawater (47 mV) and real alkaline seawater solution (58 mV) than commercial 20% Pt/C. The CV curve of the Ni@O-C/CNTs remains almost unchanged over 1000-cycle operations in both simulated alkaline seawater and real alkaline

seawater solution, demonstrating excellent cycling stability (Figure 3H). Furthermore, the long-time stability of Ni@O-C/CNTs is evaluated through chronoamperometry in simulated alkaline seawater and real alkaline seawater, respectively. As shown in Figure 3I, it can maintain stability for over 2000 hours in simulated alkaline seawater and even real alkaline seawater, demonstrating high stability in harsh environments (real alkaline seawater electrolyte).

DFT calculations. The above results indicate that Ni@O-C/CNTs exhibit higher intrinsic activity for HER than the previously reported Ni@C material⁵⁸, with oxygen doping potentially playing a significant role. To further investigate its mechanism, density functional theory (DFT) calculations were conducted to evaluate the intrinsic HER activity of Ni@O-C/CNTs in comparison with Ni@C material. As shown in Figure 4A, the charge redistribution reveals enhanced charge transfer between Ni and C atoms following oxygen doping. Additionally, density of states (DOS) calculations show that oxygen doping shifts the d-band center of nickel downward, from -1.412 eV in Ni-C to -1.484 eV in Ni@O-C (Figure 4B), thus facilitating alkaline HER.⁵⁹

The alkaline HER process involves multiple steps, including the adsorption of H₂O molecules onto the catalyst surface, the water activation to the transition state, the dissociation of H₂O into hydroxyl groups (OH⁻) and H atoms,

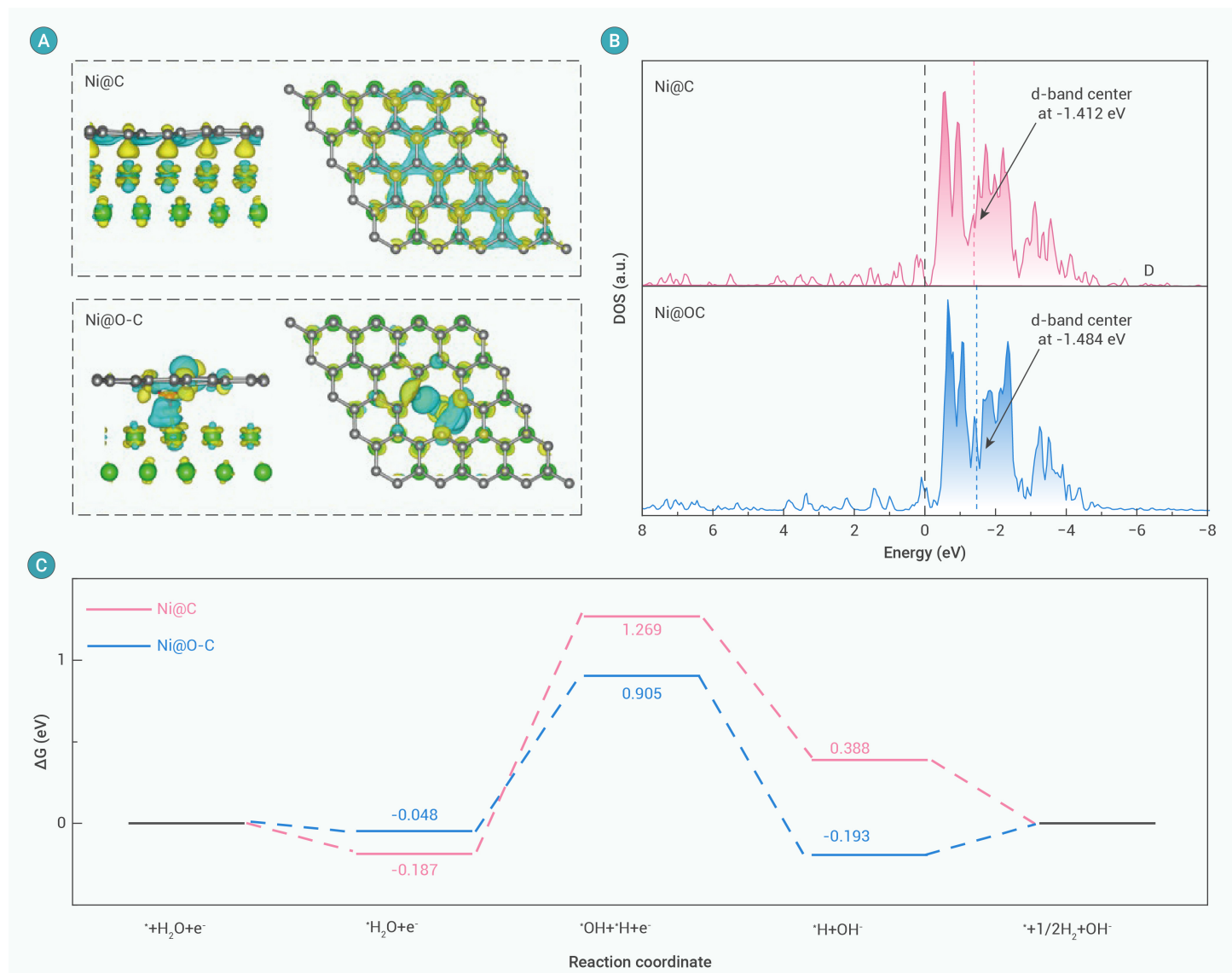


Figure 4. Theoretical analysis of electronic structure and HER mechanism (A) The charge density redistribution, (B) calculated DOS and (C) free energy diagrams for HER on Ni@C and Ni@O-C, respectively (Atoms with gray, red and green colors represent C, O and Ni atoms; in the charge density isosurface plot, blue colors show charge loss and the yellow colors show the electron gain).

the hydrogen adsorption following OH^- detachment from the surface, and the desorption of H_2 after the combination of hydrogen intermediates (H_{ads}).⁶⁰ Generally, the dissociation of water is considered a key rate-determining step in alkaline HER.⁶¹ To better elucidate each reaction step in HER, we calculate the kinetic energy barrier of each step for Ni@C and Ni@O-C during HER. The corresponding atomic configurations of Ni@O-C and Ni@C were shown in Figures S13-S14. As displayed in Figure 4C, the energy barrier for the dissociation of H_2O on Ni@O-C is 0.963 eV, significantly smaller than that of Ni@C (1.456 eV). The above results indicate that oxygen-doped Ni@O-C/CNTs samples have good HER activity in an alkaline medium.

HER performance in an MEA electrolyzer

Encouraged by the superior alkaline HER performance of the Ni@O-C/CNTs catalyst, further studies were conducted using Ni@O-C/CNTs as the cathode and commercial IrO_2 as the anode for water and seawater electrolysis in alkaline electrolytes. For this purpose, a membrane electrode assembly (MEA) electrolyzer was constructed (Figure 5A). MEA electrolyzers based on commercial Pt/C were also constructed and tested for comparison. The current-voltage curves were obtained at 60°C. Without further optimization (reactor design, membrane selection and operating conditions, etc.), the cell voltages of Ni@O-C/CNTs || IrO_2 in 1 M KOH, 1 M KOH + 0.5 M NaCl and 1 M KOH + seawater at a current density of 0.5 A cm^{-2} were 1.85 V, 1.91 V, and 2.02 V (Figure 5B), which were lower than that of commercial Pt/C || IrO_2 elec-

trolyzer (Figure S15). The corresponding energy conversion efficiencies achieved 81%, 79%, and 74%, respectively (Figure 5C). Furthermore, the long-term stability of Ni@O-C/CNTs in MEA was evaluated in real alkaline seawater by using the chronopotentiometric method (Figure 5D). The results showed that Ni@O-C/CNTs exhibited exceptional stability in real alkaline seawater for a duration exceeding 300 hours. In contrast, when physically mixed Ni nanoparticles with carbon nanotubes were used to replace Ni@O-C/CNTs and formed an electrolytic cell with IrO_2 , poor stability was observed with a lifespan of less than 30 hours during seawater electrolysis (Figure S16). This further emphasizes the indispensable role played by the unique core-shell structure of Ni@O-C/CNTs in ensuring their long-term stability during seawater electrolysis. These findings underscore the great potential of Ni@O-C/CNTs in future green hydrogen production applications.

CONCLUSION

In summary, Ni@O-C/CNTs chainmail catalysts were synthesized by a simple and cost-effective pyrolysis process of salicylate intercalated nickel hydroxides, which exhibited excellent HER activity and durability in alkaline water, simulated alkaline seawater, and real alkaline seawater. The abundant catalytic active centers, oxygen-containing groups, high specific surface area, and porous nature, provided strong modulation capabilities for promoting water molecular dissociation as well as accelerated charge/mass transfer. The unique core-shell structure enables long-term stabilization in elec-

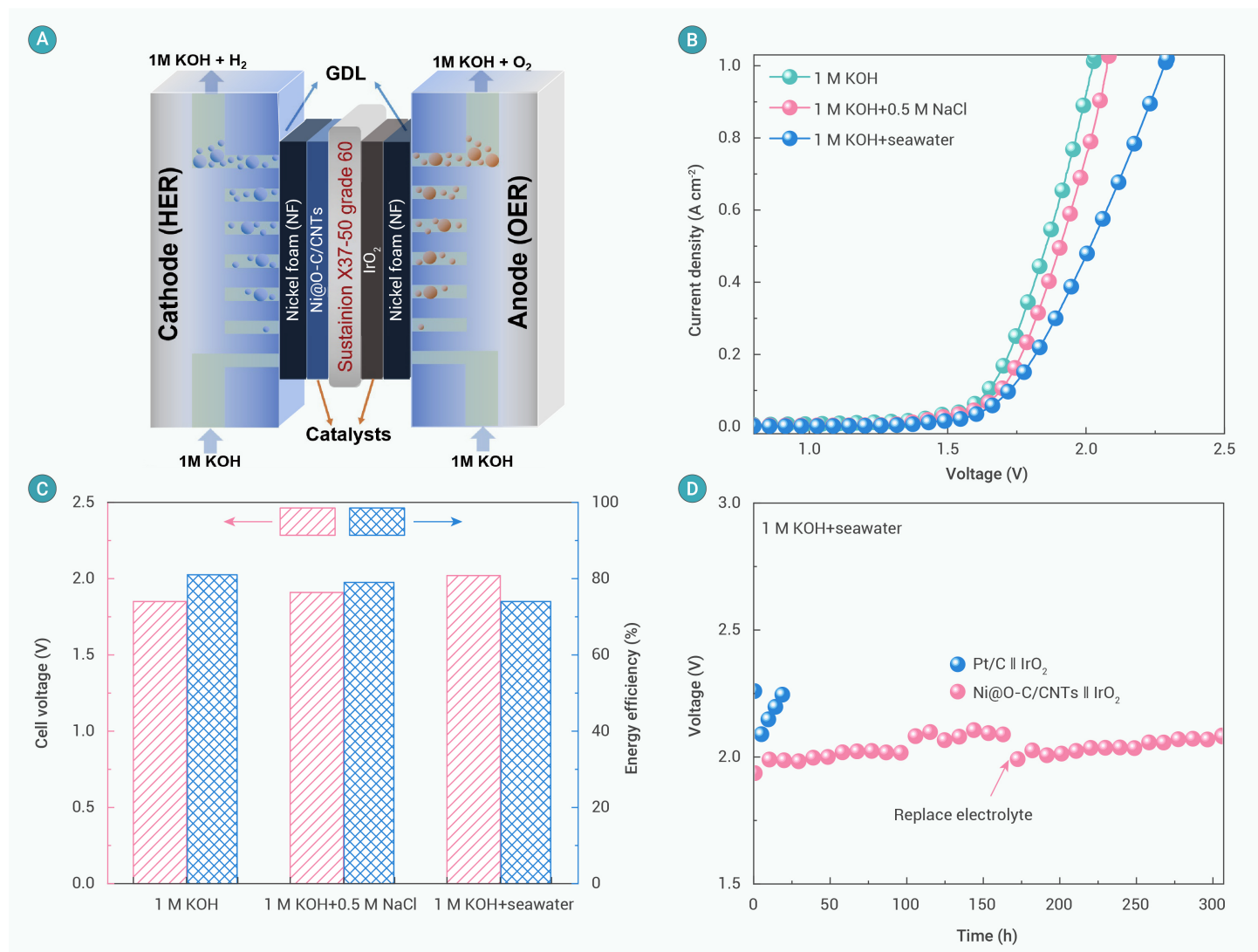


Figure 5. Alkaline HER in the MEA electrolyzer (A) Schematic diagram of MEA electrolyzer. (B) LSV curves of the MEA reactors using Ni@O-C/CNTs and IrO₂ as the cathodic and anodic electrodes in different electrolytes, respectively. (C) Cell voltage at a current density of 0.5 A cm⁻² in Figure 4B, and the corresponding energy efficiency. (D) Stability tests of the MEA water electrolyzers at the current density of 0.5 A cm⁻² at 60°C.

trolytes. Finally, Ni@O-C/CNTs were evaluated in an MEA-based electrolyzer for hydrogen production in alkaline seawater environments with promising prospects. This synthesis strategy also offers the possibility for developing other transition metal-carbon-based functional materials with similar structures.

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AUTHOR CONTRIBUTIONS

K.L.W., T.Y.Z., H.J.W. and S. L. contributed equally to this work. J.F.L., and L.Y.W. conceived the idea and supervised the project. K.L.W., H.J.W. and S. L. performed most of the experiments and analyses. C.B.X. and X.Y. conducted the DFT simulations and analyzed the results. T.Y.Z. assisted with sample characterization. K.L.W., T.Y.Z., R.L.G., S.L., Y.X.Q., Y.G., L.Y.W., and J.F.L. wrote and revised the manuscript. All authors reviewed and commented on the submitted version of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

The authors declare that the main data supporting the findings of this study are available within the paper and its supplementary information. Extra data are available on reasonable request from the corresponding author.

SUPPLEMENTAL INFORMATION

It can be found online at <https://doi.org/10.59717/j.xinn-mater.2025.100148>