Rationally Designed Ni–Ni$_3$S$_2$ Interfaces for Efficient Overall Water Electrolysis

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High-performance water-splitting electrocatalysts are needed by the energy sector for sustainable hydrogen production. Herein, it is demonstrated that the surface decoration of a nickel foam (NF) with porous Ni/Ni$_3$S$_2$ microsheets yields an electrode with high electrical conductivity and an abundance of accessible Ni$^0$–Ni$_3$S$_2$ interfaces as active sites for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). In 1 M potassium hydroxide, Ni–Ni$_3$S$_2$/NF exhibits outstanding HER activity (an overpotential of 57 mV at a current density of 10 mA cm$^{-2}$) and similarly impressive OER activity (a low overpotential of only 295 mV at a current density of 20 mA cm$^{-2}$). A water electrolyzer constructed using Ni–Ni$_3$S$_2$/NF as the HER and OER electrodes exhibits a low cell voltage of only 1.57 V with no obvious performance loss over 30 h, outperforming devices based on expensive Pt/C and RuO$_2$ catalysts. To the best of the author’s knowledge, Ni–Ni$_3$S$_2$/NF is one of the best non-precious metal electrocatalysts reported to date for overall water splitting.

1. Introduction

Dwindling fossil fuel reserves, together with environmental concerns relating to anthropogenic CO$_2$ emissions and global warming, motivate the search for new and sustainable energy carriers. Hydrogen (H$_2$) represents a promising next-generation energy carrier due to its high energy density (142 MJ kg$^{-1}$) and potential to be generated from fossil fuels, water, and biomass.\[1\] Direct electrolysis of water is widely regarded as the most sustainable way to realize large-scale H$_2$ production without CO$_2$ emissions.\[2\] However, the implementation of water electrolysis for industrial H$_2$ manufacture is hampered by the sluggish kinetics of its two half reactions, the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).\[3\] The kinetics of the HER is generally improved in acidic media, though OER kinetics often become extremely sluggish in acidic electrolytes. Hence, researchers have typically been limited to the use of platinum (Pt) and ruthenium (Ru)/iridium (Ir) oxides for HER and OER, respectively.\[4\] However, the scarcity and high cost of these precious metals handicap their industrial applications.\[5\] Thus, the realization of a “Hydrogen Economy” based on clean H$_2$ generation by water electrolysis hinges on the discovery of efficient and stable electrocatalysts for HER and OER based on earth-abundant elements, ideally first row transition metals. Currently, good progress is being made toward this goal, though improvements in electrocatalyst activity and stability are needed under the harsh operating conditions of alkaline water electrolyzers.\[6\]

In the pursuit of low-cost electrocatalysts for HER, OER, and overall water electrolysis, nickel-based electrocatalysts show particular promise due to their corrosion resistance, high activities in alkaline media, and good mechanical properties.\[7\] Recent studies have shown that Ni-based chalcogenides, especially Ni$_3$S$_2$, offer potential as bifunctional catalysts for overall water electrolysis.\[8\] However, the catalytic activity of Ni$_3$S$_2$ itself is modest, owing to its intrinsic activity and limited availability of active sites. The fabrication of heterostructured interfaces is an effective strategy for improving the HER and OER activities of heterogeneous catalysts, by facilitating the activation of key reaction species.\[7,8c,9\] For example, CoFe$_2$O$_4$/C interfaces were shown to enhance OER performance,\[10\] whereas Pt/M(OH)$_2$ and Ni/MO$_x$ (where M is a transition metal) interfaces improved HER activity.\[9b,11\] Theoretical studies have shown that Ni$_x$/NiS$_x$ interfaces offer better intrinsic activity for HER than Ni$_x$/NiO interfaces.\[12\] Furthermore, NiS/Ni interfaces offer bifunctional oxygen evolution and hydrogen evolution activity.\[13\] However, in

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that work, the NiS/Ni electrocatalyst was synthesized by sulfidation of large-size Ni nanoparticles, thus creating a limited number of metal–metal sulfide interfaces, which limited overall water electrolysis performance. In another study, presynthesized NiPt3/NiS nanoparticles were deposited on an electrode surface, with the interface resistance impeding electron transfer and limiting the reaction rates for HER.13 Synthetic strategies must be found toward electrocatalysts with abundant Ni/NiS interfaces (ideally supported by Ni foam [NF]), thus enabling efficient overall water electrolysis in alkaline media.

Considering the requirement for catalysts with high density of active sites and fast electron-transfer properties, we fabricated herein a novel electrocatalyst (Ni–NiS3/NF) comprising porous Ni/NiS2 microsheets supported on a NF. The microsheets themselves were composed of small Ni–NiS2 nanoparticles, thus offering an abundance of Ni/NiS2 interfaces for HER and OER. To ensure intimate contact between the microsheets and the NF, we used a novel in situ growth strategy to prepare Ni–NiS2/NF, comprising hydrothermal growth of Ni(OH)2 microsheets on the NF, partial sulfidation to give Ni(OH)3Sx/NF, followed by a final H2 reduction step (to reduce Ni(OH)3Sx to Ni–NiS2 nanoparticles with a heterogeneous structure). The intimate contacts between the components in Ni–NiS2/NF allowed facile electron transfer and a low charge transfer resistance, enabling outstanding HER (57 mV at a current density of 10 mA cm−2) and OER activity (295 mV at a current density of 20 mA cm−2) in alkaline media. In addition, when Ni–NiS2/NF was used as both the cathode and anode in an alkaline electrolyzer, a current density of 10 mA cm−2 was achieved at a low cell voltage of only 1.57 V with no obvious performance loss over 30 h, outperforming a RuO2(+)//20%Pt/C(−) electrolyzer under the same testing conditions.

2. Results and Discussion

The fabrication process of the heterostructured Ni–Ni3S2/NF electrode is shown in Scheme 1. Porous NF was used as the support owing to its low cost and good electrical conductivity. A hydrothermal method was first applied to grow Ni(OH)2 microsheets on the NF. The Ni(OH)2/NF electrode was then partial sulfided using Na2S, yielding a Ni(OH)3Sx/NF electrode, which was then hydrogen reduced at 450 °C to obtain the Ni–Ni3S2/NF electrode. The changes in morphology of the electrodes with each step of the process were followed by scanning electron microscopy (SEM). As shown in Figure 1a, the Ni(OH)2/NF electrode was covered by a dense layer of thin Ni(OH)2 microsheets, with the electrode retaining that 3D interconnected porous skeleton of the NF. The vertically aligned and interconnected Ni(OH)2 microsheets had an average thickness of around 30 nm and a width of around 10 μm. Following partial sulfidation of the Ni(OH)2 microsheets using a mild ion exchange reaction to form Ni(OH)3Sx/NF, the architecture of the electrode was largely unchanged (Figure S1, Supporting Information), but the color of the electrode changed from green (typical of Ni(OH)2) to black, indicating successful sulfidation.13 Following the H2 reduction step at 450 °C, the smooth Ni(OH)3Sx microsheets were transformed into a 3D porous microsheets composed of partially sintered Ni–Ni3S2 nanoparticles with a mean size of ≈30 nm (Figure 1b). The 3D porous microsheets were expected to provide an abundance of exposed interface active sites for electrocatalysis and also numerous pathways for ion and charge transport. For comparison, pure Ni3S2/NF and Ni/NF electrodes were also prepared, with their morphologies being similar to that of Ni–Ni3S2/NF (Figure S2, Supporting Information).

Powder X-ray diffraction (XRD) was used to study the crystal structure of the synthesized catalysts. To eliminate signals from the NF, the Ni–Ni3S2 nanoparticles were detached from the NF by ultrasonication, and then analyzed by XRD. The XRD pattern for Ni–Ni3S2 (Figure 1c) contained peaks due to hexagonal Ni3S2 (JCPDS no. 73-0698) and cubic Ni metal (JCPDS no. 70-0989). No other peaks were observed in the diffraction pattern that might indicate the presence of impurities. Further morphological and structural information about Ni–Ni3S2/NF was obtained by transmission electron microscopy (TEM). The TEM image of Ni–Ni3S2/NF (Figure 1d) revealed that the small nanoparticles in the Ni–Ni3S2 microsheets possessed a heterogeneous structure, with a metallic Ni and Ni3S2 being intimately connected through a well-defined interface. The TEM image shows small crystal domains (marked by dotted lines) with different lattice fringes. Figure 1e–g are high-resolution TEM (HR-TEM) images of the selected domains indicated in Figure 1d. Lattice fringes with an interplanar spacing of 2.03 Å were readily assigned to the (111) plane of metallic Ni, whereas fringes with an interplanar spacing of 2.04 and 2.87 Å were consistent with the (110) and (202) planes of Ni3S2, respectively. The intimate contact of the two heterodomains implies an abundance of Ni/Ni3S2 interfaces in the Ni–Ni3S2/NF electrode.14 The presence of the Ni metal domains was expected to boost electron transfer kinetics across microsheets to the current collector (i.e., NF).17 The selected area electron diffraction (SAED) pattern (Figure 1h) exhibited well-defined diffraction rings corresponding to the (200) and (220) planes of metallic Ni and the (116) and (202) plane of Ni3S2. The rings confirm the presence of Ni and Ni3S2.

Scheme 1. Schematic diagram showing the stepwise fabrication of the Ni–Ni3S2/NF electrode.
The mole ratio of Ni and NiS in the heterostructured Ni–NiS2 nanocrystals in the heterostructured Ni–NiS2 catalyst. Energy-dispersive X-ray (EDX) spectrometry (Figure 1i) revealed that the Ni and S were uniformly distributed over the Ni–NiS2 microsheets. The Ni and S contents in Ni–NiS2 were 93.83 and 6.16 at %, respectively.

X-ray photoelectron spectroscopy (XPS) was further applied to probe the near surface region chemical composition and element valence states in the catalysts. The high-resolution Ni 2p XPS spectrum (Figure 2a) of Ni–NiS2/NF showed a set of peaks at 852.7 and 873.4 eV in a 2:1 area ratio, which were assigned to the 2p1/2 and 2p3/2 signals, respectively, of a Ni2+ species bonded to S in NiS2 (NiS3). On the higher binding energy side of these peaks is a set of Ni2+ shake-up satellites. The sharp set of peaks at 852.7 and 870.2 eV (2:1 ratio) for Ni–NiS2 correspond to the 2p1/2 and 2p3/2 signals, respectively, of metallic Ni0. The S 2p XPS spectrum of Ni–NiS2/NF (Figure 2b) showed a doublet of peaks at the binding energies of 162.4 eV (2p1/2) and 163.8 eV (2p3/2), typical for the sulfide ion (S2−). The mole ratio of Ni and NiS2 in the active Ni/NiS2 microsheets (on NF), determined from the relative areas of Ni 2p and S 2p regions in the XPS survey spectrum, was ~1:1. The O 1s XPS spectrum of Ni–NiS2/NF (Figure S5, Supporting Information) showed a single broad peak at 331.6 eV, which was assigned to adsorbed hydroxyl groups (O(ads)) or adsorbed oxygen (Oads). For comparison, the XPS spectra of NiS2/NF and Ni/NF were also measured (Figure 2a and Figure S6, Supporting Information, respectively). The Ni 2p XPS spectrum (Figure 2a) of NiS2/NF exhibited Ni2+ peaks and associated shake-up satellites (as seen for Ni–NiS2/NF), though no Ni0 peaks. The deconvoluted S 2p XPS spectrum for NiS2/NF was also similar to that of Ni–NiS2/NF. Interestingly, the Ni 2p XPS peaks for Ni2+ (i.e., Ni–S species) and the S 2p peaks for Ni–NiS2/NF were at lower binding energies than the corresponding features for NiS2/NF. This is explained by the redistribution of charge at the interfaces arising from electronic interactions between adjacent NiS2 and Ni0 components in the heterostructured Ni–NiS2/NF.

The HER performance of the Ni–NiS2/NF electrode and selected reference electrodes (Ni/NF, NiS2/NF, and 20% Pt/C/NF) was explored in a classical three electrode system in 1.0 M potassium hydroxide (KOH) electrolyte at 25 °C. Electrochemical potentials measured versus Hg/HgO were transformed to the reversible hydrogen electrode (RHE) according to the electrode calibration relationship, \( E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.925 \) V. As shown in Figure 3a, the commercial Pt/C/NF offered the best catalytic activity for the HER at low overpotentials (15 mV to achieve a current density of 10 mA cm−2). Ni–NiS2/NF required a relatively low overpotential of 57 mV to deliver 10 mA cm−2, much better performance than Ni/NF (134 mV) and NiS2/NF (128 mV). Results demonstrate that the heterostructured Ni–NiS2 catalyst offered higher HER catalytic activity than its Ni0 and NiS2 components. More importantly, Ni–NiS2/NF exhibited a superior HER activity than 20% Pt/C when the current density exceeded 50 mA cm−2.
The HER kinetic process of Ni–Ni$_3$S$_2$/NF was studied by the Tafel plot method (Figure 3b). Ni–Ni$_3$S$_2$/NF exhibited a relatively low Tafel slope of 66 mV dec$^{-1}$ in alkaline solution, indicating that the HER proceeded via a Volmer–Heyrovsky mechanism, and electrochemical desorption was the key step controlling the HER rate.[19] The low Tafel slope of Ni–Ni$_3$S$_2$/NF was comparable to that of 20% Pt/C/NF (48 mV dec$^{-1}$), implying a smooth HER evolution process on Ni–Ni$_3$S$_2$/NF. As expected, Tafel slopes were higher for Ni/NF (134 mV dec$^{-1}$) and Ni$_3$S$_2$/NF (128 mV dec$^{-1}$). The fact that the Tafel slopes were greater than 120 mV dec$^{-1}$ implies that water dissociation was the rate-determining step (RDS) for the HER on their surface. These results demonstrate that water dissociation can be greatly accelerated by the Ni–Ni$_3$S$_2$ interfaces, thereby improving the HER rate.[20] The reaction kinetics of HER on Ni–Ni$_3$S$_2$/NF and the other electrodes were further investigated by electrochemical impedance spectroscopy (EIS). Nyquist plots obtained from the EIS data are shown in Figure 3c, with the fitted equivalent circuits provided as insets. The charge transfer resistance ($R_d$) of Ni–Ni$_3$S$_2$/NF (2.4 Ω) was significantly smaller than those of Ni/NF (51.5 Ω) and Ni$_3$S$_2$/NF (39.1 Ω), indicating faster electron transfer during HER on Ni–Ni$_3$S$_2$/NF compared with the other electrodes.

Next, the OER performance of Ni–Ni$_3$S$_2$/NF and the other reference electrodes including Ni/NF, Ni$_3$S$_2$/NF, and RuO$_2$/NF were evaluated. As shown in Figure 3d, the heterostructured Ni–Ni$_3$S$_2$/NF electrode displayed excellent OER activity, delivering an ultralow overpotential of 295 mV at a current density of 20 mA cm$^{-2}$, which was lower than the overpotentials required by the other electrodes to achieve the same current density: Ni/NF (423 mV), Ni$_3$S$_2$/NF (340 mV), and RuO$_2$/NF (355 mV). As expected, Ni–Ni$_3$S$_2$/NF delivered a lower OER Tafel slope (99 mV dec$^{-1}$) than the other electrodes: Ni/NF (113 mV dec$^{-1}$), Ni$_3$S$_2$/NF (125 mV dec$^{-1}$), and RuO$_2$/NF (118 mV dec$^{-1}$). Results confirm fast OER kinetics on the Ni–Ni$_3$S$_2$/NF surface (Figure 3e). The Nyquist plots (Figure 3f) showed a small charge-transfer resistance ($R_d$) of only 1.4 Ω for Ni–Ni$_3$S$_2$/NF, much smaller than the corresponding values for Ni/NF (3.7 Ω) and Ni$_3$S$_2$/NF (2.6 Ω). The test data suggest that the Ni–Ni$_3$S$_2$/NF is an excellent electrocatalyst for the OER.

To explore the intrinsic reasons for outstanding bifunctional HER and OER activity of the Ni–Ni$_3$S$_2$/NF electrode, we first calculated the electrochemically active surface area (ECSA) for the different catalysts by the double-layer capacitance ($C_{dl}$) method. In general, the catalyst with the largest ECSA will offer the most active sites and deliver the highest electrocatalytic performance. The $C_{dl}$ value of Ni–Ni$_3$S$_2$/NF (36 mF cm$^{-2}$) was similar to that of Ni$_3$S$_2$/NF (37 mF cm$^{-2}$), and around half that of Ni/NF (62 mF cm$^{-2}$). This result indicates that the enhanced activity of Ni–Ni$_3$S$_2$/NF was not due to an increased availability of active sites, but rather the type of active site (in particular, the Ni–Ni$_3$S$_2$ heterojunctions in Ni–Ni$_3$S$_2$/NF). The conductivity of the different catalysts was further investigated, as the reaction rate of semiconducting catalysts is often limited by the rate of electron supply.[21] The intrinsic conductivity of pure Ni and Ni$_3$S$_2$ catalysts was probed by calculating the density of states (DOS) near the Fermi level. For Ni$_3$S$_2$, two wide bandgaps were seen in the DOS plot, consistent with the semiconducting properties of Ni$_3$S$_2$ (Figure 3g). For metallic Ni, the DOS plot showed occupancy of d-orbitals up to the Fermi level (Figure 3h). Hence, electron transfer at the heterostructured Ni–Ni$_3$S$_2$ interfaces would have approached that of metallic Ni (because the Ni–Ni$_3$S$_2$ nanoparticles had a large Ni core and thin Ni$_3$S$_2$ shell). The actual resistance of the catalysts was tested using an impedance/gain-phase analyzer coupling system.[22] The resistance values determined for Ni, Ni$_3$S$_2$, and Ni–Ni$_3$S$_2$ powders were 0.016, 0.05, and 0.028 Ω, respectively. Results confirm that the Ni–Ni$_3$S$_2$ possessed a conductivity close to metallic Ni, which was highly beneficial to the electrocatalytic reactions.
Given that Ni–Ni$_3$S$_2$/NF demonstrated remarkable electrocatalytic activity for both HER and OER in an alkaline electrolyte, the overall electrocatalytic water electrolysis performance of Ni–Ni$_3$S$_2$/NF was studied by integrating the free-standing bifunctional electrode as the anode and cathode in a two-electrode electrolyzer. As shown in Figure 4a, the Ni–Ni$_3$S$_2$/NF||Ni–Ni$_3$S$_2$/NF water electrolyzer required a small cell voltage of 1.57 V at a current density of 10 mA cm$^{-2}$, which is lower than the cell voltage of a RuO$_2$(+)||20% Pt/C(-) system (1.63 V). The activity of the Ni–Ni$_3$S$_2$/NF electrode is comparable to the best reported sulfide-based electrocatalysts for water splitting in alkaline conditions (Table S3, Supporting Information). Furthermore, the experimentally measured H$_2$ and O$_2$ yields closely matched the theoretical values, with the Faradaic efficiency of the Ni–Ni$_3$S$_2$/NF-based electrolyzer being around 97.8% (Figure 4b). The durability of a catalyst is a further important factor when evaluating overall performance. The alkaline electrolyzer fabricated using Ni–Ni$_3$S$_2$/NF offered a smooth curve with negligible degradation over 30 h at a constant current density of 10 mA cm$^{-2}$ (Figure 4c), implying excellent catalyst stability for both HER and OER. SEM confirmed that the Ni–Ni$_3$S$_2$/NF electrode retained its structural integrity during long-term electrolysis in an aggressive alkaline electrolyte (Figure S7, Supporting Information). In a sharp contrast, the RuO$_2$(+)||20% Pt/C(-) electrolyzer rapidly lost electrocatalytic activity with use, which is explained by the electrocatalyst peeling off the NF during operation at high currents.

3. Conclusion

In conclusion, we successfully fabricated heterostructured Ni–Ni$_3$S$_2$/NF electrodes, which demonstrate outstanding activity for HER and OER in alkaline media. The electrodes possess
the porous 3D network structure of the supporting NF ensuring good mass transport, and are covered by porous microsheets composed of heterostructured Ni-Ni$_3$S$_2$ nanoparticles. This architecture imparted the electrodes with high electrical conductivity and an abundance of accessible active sites. The Ni-Ni$_3$S$_2$/NF electrode delivered an HER overpotential of 57 mV at 10 mA cm$^{-2}$ in 1 M KOH, and a very low OER overpotential of 295 mV at 20 mA cm$^{-2}$, comparable to the best nickel-based catalysts developed to date for overall water electrolysis. An alkaline electrolyzer fabricated using Ni-Ni$_3$S$_2$/NF as the anode and the cathode delivered excellent performance (a potential of only 1.57 V was needed to realize a current density of 10 mA cm$^{-2}$) and good stability.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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