Exceptional Performance of Hierarchical Ni–Fe (hydr) oxide@NiCu Electrocatalysts for Water Splitting

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Developing low-cost bifunctional electrocatalysts with superior activity for both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) is of great importance for the widespread application of the water splitting technique. In this work, using earth-abundant transition metals (i.e., nickel, iron, and copper), 3D hierarchical nanoarchitectures, consisting of ultrathin Ni–Fe layered-double-hydroxide (Ni–Fe LDH) nanosheets or porous Ni–Fe oxides (NiFeOx) assembled to a metallic NiCu alloy, are delicately constructed. In alkaline solution, the as-prepared Ni–Fe LDH@NiCu possesses outstanding OER activity, achieving a current density of 10 mA cm\(^{-2}\) at an overpotential of 218 mV, which is smaller than that of RuO\(_2\) catalyst (249 mV). In contrast, the resulting NiFeO\(_x\)@NiCu exhibits better HER activity, yielding a current density of 10 mA cm\(^{-2}\) at an overpotential of 66 mV, which is slightly higher than that of Pt catalyst (53 mV) but superior to all other transition metal (hydr)oxide-based electrocatalysts. The remarkable activity of the Ni–Fe LDH@NiCu and NiFeO\(_x\)@NiCu is further demonstrated by a 1.5 V solar-panel-powered electrolyzer, resulting in current densities of 10 and 50 mA cm\(^{-2}\) at overpotentials of 293 and 506 mV, respectively. Such performance renders the as-prepared materials as the best bifunctional electrocatalysts so far.

The ever-increasing consumption of fossil fuels and resultant environmental issues, such as global warming, ozone layer depletion, and acid rains, necessitate searching for clean energy sources.[1] Hydrogen is considered to be a promising alternative to fossil fuels by virtue of its high energy density and environmental-friendliness.[2] Renewable energy (such as electricity produced from photovoltaics and wind farms) powered water splitting provides an attractive method for sustainable production of hydrogen.[3] However, the two half electrochemical reactions involved in a water splitting process, namely, the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), are kinetically sluggish, leading to significant electrode overpotentials, and thus requires efficient electrocatalysts to improve energy efficiency.[3] Currently, precious-metal-based electrocatalysts, such as Ir/Ru for OER and Pt for HER, could realize low overpotentials for water splitting. Unfortunately, the scarcity and high cost of these precious metals greatly prohibit their widespread applications. To this end, efforts have been devoted to searching for low-cost alternatives[4–8] and numerous transition-metal (hydr) oxides,[9–13] sulfides,[14–17] carbides,[18–20] phosphides,[21–23] and even carbon-based materials[24–26] have so far been studied for HER/OER. In particular, the (hydr)oxides of nickel,[27–29] iron,[30–32] cobalt,[33–35] and copper[36] have been reported as efficient HER and/or OER electrocatalysts. For instance, Gong et al. fabricated an electrolyzer using a nickel oxide/nickel supported by carbon nanotubes and Ni–Fe layered double hydroxide (LDH) as HER and OER electrocatalysts, respectively.[37] The resulting electrolyzer yielded a current density of 20 mA cm\(^{-2}\) at a voltage of 1.5 V. In addition, Luo et al. constructed a perovskite solar cell powered an electrolyzer using a bifunctional Ni–Fe LDH electrocatalyst for both OER and HER in alkaline electrolyte.[38] They obtained a solar-to-hydrogen efficiency of 12.3% at a photocurrent density of 10 mA cm\(^{-2}\) from the apparatus.

For the practical applications, integrating cathodic and anodic electrodes in an electrolyzer with the same electrolyte is highly beneficial for increasing energy efficiency and reducing fabrication cost.[39] Unfortunately, it is always challenging to couple HER and OER in the same electrolyte due to the incompatibility of the catalyst stability and activity. Recently, developing bifunctional electrocatalysts which possess high activity for both HER and OER has proved to be a promising route for overall water splitting.[40–45] For instance, Jia et al. assembled single-layered NiFe-LDH nanosheets on defective graphene. The resulting bifunctional catalyst yielded a current density of 20 mA cm\(^{-2}\) at a voltage of 1.5 V, which represents the highest activity for overall water splitting to date.[42]
Luo et al. synthesized a bifunctional electrocatalyst, consisting of Cu nanowires shelled with NiFe-LDH nanosheets. It produced current densities of 10 and 100 mA cm\(^{-2}\) at potentials of 1.54 and 1.69 V, respectively.\(^{[42]}\)

Despite numerous efforts devoted to exploring earth-abundant transition metal-based catalysts, high-performance bifunctional HER/OER electrocatalysts are still scarce. Critical issues related with transition metal (hydr)oxide electrocatalysts lie in the limited number of active sites and poor conductivity, leading to unsatisfactory performance for water splitting.\(^{[27]}\) Note that the activity of metal (hydr)oxides could be greatly enhanced by delicately engineering their nanostructures. Herein, using earth-abundant transitional metal elements including nickel, iron, and copper, the authors constructed 3D core–shelled architectures, consisting of NiFe-LDH nanosheets/porous NiFe oxides assembled to a metallic NiCu alloy, as bifunctional electrocatalysts for overall water splitting. The focus of this study is to optimize the activity of the catalysts by engineering their nanostructures. The prominent structural feature of the as-prepared catalysts lies in the presence of abundant heterogeneous nanointerfaces, endowing with not only the merits of the individual constituents, but also their synergistic effects in HER and OER processes. In addition, the assembly of ultrathin NiFe-LDH nanosheets or porous NiFe oxides onto the metallic NiCu could afford large surface areas, fast electron transfer, facile access to electrolyte, and release of gas bubbles. Benefiting such structural merits, the as-prepared materials show excellent activity for both OER and HER. The outstanding performance for water splitting was demonstrated by a 1.5 V solar-panel-powered electrolyzer, yielding current densities of 10 and 50 mA cm\(^{-2}\) at overpotentials of 293 and 506 mV, respectively.

The synthesis protocol starts from the NiCu nanoparticles which were synthesized via a polyol-assisted reduction process (see the details in the Experimental Section). The resulting NiCu nanoparticles have diameters of ca. 21 ± 4 nm (see Figure S1, Supporting Information). X-ray diffraction (XRD) pattern of the NiCu nanoparticles (see Figure S2, Supporting Information) shows one set of diffraction peaks, which can be well indexed by JCPDS #04-0850, indicating the formation of NiCu alloy. Using the NiCu nanoparticles as seeds, NiFe-LDH@NiCu was obtained via self-assembly of NiFe-LDH nanosheets. The morphological structures of the as-prepared NiFe-LDH@NiCu were studied by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) as shown in Figure 1. FESEM images (see Figure 1a–c) reveal that the resulting NiFe-LDH@NiCu possesses a 3D hierarchical structure, consisting of numerous nanosheets self-assembled into quasi-spheres with diameters of 400–600 nm. TEM images (see Figure 1d, e) show clear contrast between the center and

![Figure 1.](image)
periphery of the NiFe-LDH@NiCu nanoparticles, manifesting the formation of core–shell structure. The formation of such a core–shell structure is related to the synthesis protocol, which involves seed (NiCu nanoparticles) mediated growth of NiFe-LDH. High-resolution TEM image (see Figure 1f) shows a bilayered nanosheet with a thickness of ca. 1.6 nm. The average thickness between layers is estimated to be 0.8 nm, which is well matched with the spacing value of NiFe-LDH (003) planes. High-angle annular dark field scanning TEM (HAAD-STEM) image (see Figure 1g) and corresponding electron energy loss spectroscopy (EELS) images (see Figure 1h–k) vividly resolve the distribution of Fe, Cu, Ni, and O elements. Notably, no other elements were detected from the sample, indicating its high purity. The crystallographic structure of the as-prepared NiFe-LDH@NiCu was examined by XRD. The diffraction peaks in the XRD profile can be well ascribed to cubic NiCu alloy phase (JCPDS #04-0850) and α-phase Ni(OH)₂ (JCPDS #038-0715 which is the same as NiFe-LDH) as shown in Figure S3 in the Supporting Information. Compared with β-phase NiFe-LDH, α-phase NiFe-LDH is a more active OER electrocatalyst. [33]

NiFe-LDH@NiCu was transformed into NiFeOₓ@NiCu by a simple thermal treatment. Figure 2 shows the morphological structures of the resulting NiFeOₓ@NiCu. Interestingly, the NiFeOₓ@NiCu shows different morphology compared with the NiFe-LDH@NiCu sample. FESEM images (see Figure 2a–c) show that the NiFeOₓ@NiCu exhibits a well-defined spherical structure. TEM image (see Figure 2d) further indicates that the surface of the NiFeOₓ@NiCu nanospheres is relatively smooth. HRTEM image (see Figure 2e) shows distinct lattice fringes with spacing values of 0.2 and 0.24 nm, corresponding to the interdistance of NiFeOₓ (021) and (101) planes, respectively. HAAD-STEM image (see Figure 2f) clearly reveals a porous structure of the NiFeOₓ@NiCu nanosphere. The formation of porous structure could be attributed to the dehydration process at high temperatures. The distribution of Ni, Fe, Cu, and O elements is also studied by HAAD-STEM (see Figure 2g) and EELS mapping images (see Figure 2h–k). The XRD pattern of the NiFeOₓ@NiCu sample is shown in Figure S4 in the Supporting Information. The diffraction peaks can be well assigned to NiCu alloy phase (JCPDS #04-0850) and NiFeOₓ phase (JCPDS #44-1159). For comparison, NiFe-LDH sample was also synthesized. Shown in Figure S5 in the Supporting Information, the morphology of the NiFe-LDH sample is similar to that of NiFe-LDH@NiCu, consisting of ultrathin nanosheets self-assembled into large aggregates. Herein, it should be pointed out that the formation mechanism of the two materials is different. The formation of the NiFe-LDH@NiCu nanoarchitectures is attributed to the seed mediated growth process. In contrast, the hierarchical structure of the NiFe-LDH is related to the self-assembly process, in which ultrathin NiFe-LDH nanosheets are spontaneously aggregated to reduce the total surface energy. The morphology of the NiFe-LDH is further examined by atomic force microscopy as shown in Figure S6 in the Supporting Information. It indicates that the NiFe-LDH sample consists

Figure 2. a–c) FESEM, d, f) TEM, f, g) HAADF-STEM images of NiFeOₓ@NiCu, and corresponding EELS mapping of h) iron, i) nickel, j) copper, and k) oxygen.
of numerous nanosheets aggregates, which is consistent with the TEM observation. The thickness of the NiFe-LDH was estimated to 2.4 nm, corresponding to a trilayered nanosheet. XRD analyses indicate that the resulting NiFe-LDH possesses an identical phase structure of $\alpha$-Ni(OH)$_2$ (JCPDS 038–0715) as shown in Figure S7 in the Supporting Information. The composition of the samples was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) as listed in Table S1 in the Supporting Information. It should be pointed out that the content of oxygen in the sample was estimated by subtracting the total mass of the sample with those of metals, and that the results were carefully checked for reproducibility.

To analyze the electronic structures of the samples, X-ray photoelectron spectroscopy (XPS) tests were conducted. Figure S8a–c in the Supporting Information show the Ni 2p, Fe 2p, and Cu 2p core level spectra of the samples, respectively. All the spectra were corrected using the C 1s signal located at 284.5 eV and then carefully fitted using the software XPSpeak41. To decompose the XPS spectra, the constraints of equal spin–orbit splitting for the peaks in binding energy (BE), peak area, and full width at half-maximum were thoroughly considered. The spectra consist of doublets of 3/2 and 1/2, and each doublet contains a major and a satellite peak. An inspection on the spectra could reveal distinct shifts in the BE of the elements. For instance, for Ni 2p 3/2, the NiCu sample exhibits a BE value of 854.2 eV. Such a BE value is higher than that of metallic nickel (852.9 eV), which could probably be attributed to the surface oxidation of the NiCu nanoparticles. The BE value of the NiFe-LDH and NiFe-LDH@NiCu (855.6 eV) is slightly lower than that of pure Ni(OH)$_2$ (856.0 eV), which could be related to the electron transfer arisen from the introduction of Fe in the sample. The NiFeO$_x$@NiCu has a BE value of 855.1 eV, which is a typical value of Ni$^{2+}$ in the oxide state. For Fe 2p 3/2, the NiFe-LDH has a BE value of 711.6 eV, which is larger than those of NiFeO$_x$@NiCu (710.2 eV) and NiFe-LDH@NiCu (710.1 eV). More interestingly, the profiles of the Fe 2p spectra of the three samples are quite different. For Cu 2p 3/2, the BE value of NiCu (932.4 eV) is lower than those of NiFeO$_x$@NiCu (933.3 eV) and NiFe-LDH@NiCu (933.9 eV). The XPS results suggest that the electronic structures of the elements are different in the samples owing to the coupling interaction. The surface composition of the catalysts was also analyzed by XPS as shown in Table S2 in the Supporting Information. The surface NiCu nanoparticles consist of 28.9% oxygen due to the surface oxidation. The surface Ni/Cu ratio is estimated to be 2.76, which is lower than the bulky Ni/Cu ratio (3.01) as determined by ICP-AES, indicating the surface segregation of copper in the sample. In the NiFe-LDH sample, the surface Ni/Fe ratio is determined to be 3.875, which is larger than the bulky Ni/Fe ratio (3.185). It is noteworthy that the contents of copper in the surfaces of the NiFeO$_x$@NiCu and NiFe-LDH@NiCu samples are considerably lower than the bulky Cu contents, which could be explained from their core–shell structure.

The OER activity of the as-prepared catalysts was characterized in O$_2$-saturated 1.0 M KOH solution and benchmarked against that of a commercial RuO$_2$ catalyst. Figure 3a shows the polarization curves of the catalysts recorded at a scan rate of 5 mV s$^{-1}$. The RuO$_2$, NiCu, NiFe-LDH, NiFe-LDH@NiCu, and NiFeO$_x$@NiCu exhibited onset potentials of 30, 121, 144, 96, and 76 mV, respectively. Among the five catalysts, the NiFe-LDH@NiCu exhibits the highest geometric current densities. For clarity, Figure 3b comparatively shows the overpotentials at current densities of 10 and 20 mA cm$^{-2}$. To gain a geometric current density (j) of 10 mA cm$^{-2}$, the NiFe-LDH@NiCu requires an overpotential of 218 mV, which is smaller than those of 249, 265, 316, and 327 eV for the RuO$_2$, NiFe-LDH, NiFeO$_x$@NiCu, and Cu@NiFe-LDH samples, respectively. Such an overpotential is only slightly higher than those of other LDH-based catalysts reported in the literature as shown in Table S3 in the Supporting Information, rendering the resulting NiFe-LDH@NiCu a competitive candidate for OER.
as one of the best OER electrocatalysts. Interestingly, at a current density of 20 mA cm$^{-2}$, the overpotential of the NiFe-LDH catalyst (300 mV) is smaller than that of the RuO$_2$ (307 eV), manifesting that the NiFe-LDH outperforms the RuO$_2$ at high current densities, which can be evidenced from the polarization curves shown in Figure 3a. To further compare the activity, the current densities of the catalysts at an overpotential of 320 mV are shown in Figure S9 in the Supporting Information. It shows that the current densities of the catalysts follow the sequence of NiFe-LDH@NiCu (44.9 mA cm$^{-2}$) > NiFe-LDH (28.5 mA cm$^{-2}$) > RuO$_2$ (23.5 mA cm$^{-2}$) > NiFeO$_x$@NiCu (10.5 mA cm$^{-2}$) > NiCu (9.0 mA cm$^{-2}$). For better comparison, the mass-normalized current densities of the catalysts are calculated as shown in Figure S10 in the Supporting Information. It shows that among the five catalysts, the NiFe-LDH@NiCu also possesses the highest mass-normalized current density. Specifically, at an overpotential of 300 mA, the NiFe-LDH@NiCu catalyst has a mass-normalized current density of 429.1 A g$^{-1}$, which is 4.72, 4.29, 1.85, and 1.74 times those of the NiCu, NiFeO$_x$@NiCu, RuO$_2$, and NiFe-LDH, respectively. Such a remarkable mass-normalized current density of the NiFe-LDH@NiCu is also larger than those of $\gamma$CoOOH (66.6 A g$^{-1}$),$^{47}$ NiFeMo alloy (113 A g$^{-1}$),$^{39}$ Ni$_{0.6}$Fe$_{0.4}$O$_2$H$_2$ film (140 A g$^{-1}$),$^{48}$ CoMn LDH (159 A g$^{-1}$),$^{31}$ and NiFe-LDH nanoparticles (200 A g$^{-1}$) at an overpotential of 260 mV$^{40}$ reported in the literature. To study the intrinsic activity, turnover frequencies (TOFs) of the catalysts were calculated by assuming that nickel is considered as the active sites in the catalysts. As shown in Figure 3c, the TOF values of the catalysts follow the order of RuO$_2$ > NiFe-LDH@NiCu > NiFe-LDH > NiFeO$_x$@NiCu > NiCu at overpotentials less than 0.35 V. When the overpotentials are over 0.35 V, the order changes into NiFe-LDH > RuO$_2$ > NiFe-LDH@NiCu > NiFeO$_x$@NiCu > NiCu. Specifically, at an overpotential of 350 mA, the NiFe-LDH@NiCu possesses a TOF value of 0.341 s$^{-1}$, which is slightly smaller than those of RuO$_2$ (0.344 s$^{-1}$) and NiFe-LDH (0.344 s$^{-1}$), but larger than those of NiCu (0.034 s$^{-1}$) and NiFeO$_x$@NiCu (0.064 s$^{-1}$). Such a TOF value of the NiFe-LDH@NiCu is only next to that of NiFe/LDH/CNT (0.56 s$^{-1}$) but much larger than those of exfoliated NiCo LDH (0.011 s$^{-1}$),$^{50}$ CoMn LDH (0.075 s$^{-1}$),$^{31}$ and NiFeO$_x$ (0.21 s$^{-1}$)$^{12}$ reported in the literature. Figure 3d shows the Tafel plots of the catalysts. The NiFe-LDH possesses a Tafel slope of 53.0 mV dec$^{-1}$, which is close to that of the NiFe-LDH@NiCu (56.9 mV dec$^{-1}$) and much smaller than those of RuO$_2$ (100.3 mV dec$^{-1}$), NiFeO$_x$@NiCu (157.2 mV dec$^{-1}$), and NiCu (218.6 mV dec$^{-1}$), indicating the faster OER kinetics. The durability of the catalysts was evaluated by chronoamperometry tests at a current density of 10 mA cm$^{-2}$ as shown in Figure S11 in the Supporting Information. Overall, the overpotentials of the catalysts show slight increase during the testing time, suggesting that the catalysts exhibit good stability for the OER process. The durability of the NiFe-LDH@NiCu catalyst was further characterized by chronoamperometric measurements as shown in Figure 3e. At overpotentials of 250 and 300 mA, the current densities are quite stable, further verifying the excellent durability of the NiFe-LDH@NiCu catalyst. The morphology of the spent NiFe-LDH@NiCu after the chronoamperometric tests was observed by FESEM. Shown in Figure S12a, b in the Supporting Information, the spent NiFe-LDH@NiCu well preserves the 3D hierarchical structure. The XRD profiles of the pristine and spent NiFe-LDH@NiCu samples also showed negligible variations as evidence from Figure S12c in the Supporting Information.

To explore the origin of the superior activity of the NiFe-LDH@NiCu catalyst, the double-layer capacitance ($C_{dl}$) of the catalyst, which is well correlated with its electrochemical active surface area (ECSA)$^{33}$ was determined by cyclic voltammetry (CV) measurements. Figure S13 in the Supporting Information shows the CV curves recorded in the potentials ranging from 0.4 to 0.6 V and the corresponding capacitive currents ($j_c - j_{cap}/2$) as a function of scan rate. The capacitive currents possess a linear relationship with scan rate and the slope of the curve corresponds to the $C_{dl}$ of the catalyst. The NiFe-LDH@NiCu possesses a $C_{dl}$ value of 1.78 mF cm$^{-2}$, which is larger than those of NiCu (0.31 mF cm$^{-2}$), NiFeO$_x$@NiCu (1.24 mF cm$^{-2}$), and RuO$_2$ (0.37 mF cm$^{-2}$), but smaller than that of NiFe-LDH (2.16 mF cm$^{-2}$), suggesting that the ECSA is not the only reason for the superior activity of the NiFe-LDH@NiCu. To gain deep insight into the activity of the NiFe-LDH@NiCu, electrochemical impedance spectroscopy (EIS) tests were performed. The resulting Nyquist plots are shown in Figure 3f. The values of charge-transfer resistance ($R_{ct}$) of the catalysts are determined to be 7.3, 7.5, 17.4, 22.6, and 48.6 Ω for the NiFe-LDH@NiCu, RuO$_2$, NiFe-LDH, NiFeO$_x$@NiCu, and NiCu catalysts, respectively. The smallest $R_{ct}$ values of the NiFe-LDH@NiCu catalyst suggests the fastest OER kinetics, which could be attributed to the synergistic effects of NiFe-LDH shell and metallic NiCu core. Importantly, the Nyquist plot of the spent NiFe-LDH@NiCu catalyst after the chronoamperometric measurements show negligible variations as shown in Figure S14 in the Supporting Information, manifesting the excellent OER durability of the catalysts.

Apart from the OER performance, the HER performance of the catalysts was also evaluated. For comparison, the activity of the catalysts was benchmarked against a precious Pt catalyst. Shown in Figure 4a, the HER activity of the catalysts follows the sequence of Pt plate > NiFeO$_x$@NiCu > NiCu > NiFe-LDH@NiCu > NiFe-LDH. The onset potentials of the Pt, NiCu, NiFe-LDH, NiFe-LDH@NiCu, and NiFeO$_x$@NiCu were determined to be 3, 21, 49, 16, and 11 mV, respectively. To achieve a geometric current density of 10 mA cm$^{-2}$, the NiFeO$_x$@NiCu catalyst requires an overpotential of 66 mV, which is slightly higher than that of Pt plate (53 mV) and lower than those of NiCu (95 mV), NiFe-LDH@NiCu (112 mV), and NiFe-LDH (245 mV) as shown in Figure S15 in the Supporting Information. To the best of the authors’ knowledge, such a low overpotential of the NiFeO$_x$@NiCu is a record for the transitional metal (hydr)oxide-based HER catalysts as shown in Table S4 in the Supporting Information. Figure 4b shows the Tafel plots of the catalysts. The NiFeO$_x$@NiCu possesses a Tafel slope of 67.8 mV dec$^{-1}$, which is slightly larger than that of Pt plate (44.2 mV dec$^{-1}$), but much larger than those of NiCu (136.2 mV dec$^{-1}$), NiFe-LDH@NiCu (168.2 mV dec$^{-1}$), and NiFe-LDH (194.2 mV dec$^{-1}$), indicating the faster reaction kinetics. The HER stability of the catalysts was characterized by chronoamperometric measurements at an applied potential of 100 mV as shown in Figure S16 in the Supporting Information. It shows that the current densities only slightly decrease in the initial periods of testing.
time (ca. 100 min) and then remain constant with increasing time, suggesting the good HER durability of the catalysts. The chronoamperometric curves of the NiFeOx@NiCu recorded at applied potentials of 100 and 150 mV are comparatively shown in Figure 4c. At an overpotential of 150 mV, the NiFeOx@NiCu exhibits a stable current density of 49.3 mA cm\(^{-2}\), which is much higher than that of 23.9 mA cm\(^{-2}\) at an overpotential of 100 mV. These chronoamperometric results are consistent with the polarization curves shown in Figure 4a. After the chronoamperometric tests, the morphology of the spent NiFeOx@NiCu was also observed by FESEM as shown in Figure S17a, b in the Supporting Information. It indicates that the spherical structure is well maintained after the long-term HER tests. The diffraction peaks of the spent samples can be also matched with those of the pristine samples.

To reveal the HER kinetics of the catalysts, ESI measurements were conducted at an overpotential of 150 mV. The Nyquist plots in Figure 4d reveal that the NiFeOx@NiCu exhibits an ohmic resistance \((R_c)\) of 0.42 Ω, which is larger than those of Pt plate (0.08 Ω) and NiCu (0.36 Ω), but smaller than those of NiFe-LDH@NiCu (0.89 Ω) and NiFe-LDH (1.21 Ω), manifesting that the presence metallic NiCu in the catalysts enhances the conductivity. In addition, the NiFeOx@NiCu has an \(R_{ct}\) value of 7.2 Ω, which is larger than that of Pt plate (5.1 Ω), but smaller than those of NiCu (7.3 Ω), NiFe-LDH@NiCu (25.3 Ω), and NiFe-LDH (29.6 Ω), suggesting the facile charge transfer in the NiFeOx@NiCu catalyst. After the chronoamperometric tests, the \(R_c\) and \(R_{ct}\) values of the spent NiFeOx@NiCu catalyst increase as shown in Figure S18 in the Supporting Information. This could be probably attributed to the isolation of catalyst nanoparticles from the electrode due to the bubbling of hydrogen gas.

The results suggest that the NiFe-LDH@NiCu exhibits the best OER activity, while the NiFeOx@NiCu shows the superior HER activity. Inspired by their outstanding performance, the authors employed these two electrocatalysts to construct an electrolyzer for water splitting. For comparison, the reference anodic catalyst, i.e., RuO\(_2\) and the reference cathodic catalyst, i.e., Pt/C were also used and the performance of four catalyst pairs including I) RuO\(_2\)(+)|NiFeOx@NiCu(−), II) RuO\(_2\)(+)|Pt(−), III) NiFe-LDH@NiCu(+)|Pt(−), and IV) NiFe-LDH@NiCu(+)|NiFeOx@NiCu(−) were evaluated. For the overall water splitting, the catalyst pairs of I), II), III), and IV) had onset potentials of 63, 52, 129, and 117 mV, respectively. Shown in Figure 5a, the combination (III) outperforms the three another catalyst pairs at potentials less than 1.67 V. When the potential is over 1.67 V, the combination (IV) possesses the highest current densities for water splitting. For clarity, Figure S19 in the Supporting Information shows the overpotentials of the catalyst combinations at current densities of 10 and 50 mA cm\(^{-2}\). A current density of 10 mA cm\(^{-2}\) is obtained from the combinations (I), (II), (III), and (IV) at potentials of 1540, 1528, 1503 and 1523 mV, respectively. Such performance of these electrolyzers outperforms most of the electrolyzers reported in the literature as shown in Table S5 in the Supporting Information. In particular, the electrolyzers constructed with the catalyst combinations (III) and (IV) have had the second-best performance to date, only next to the electrolyzer integrated with an NiFe-LDH-NS@DG electrocatalyst.\(^{[41]}\) In contrast, to achieve a current density of 50 mA cm\(^{-2}\), the potentials increase to 1976, 1853, 178,2 and 1736 mV for the combinations (I), (II), (III), and (IV), respectively. Since large current densities are economically favorable for water splitting, the combination (III) is more feasible for

Figure 4. HER performance of the catalysts in 1 m KOH. a) HER polarization curves, b) corresponding Tafel plots, c) chronoamperometric curves of NiFeOx@NiCu recorded at overpotentials of 100 and 150 mV, and d) ESI Nyquist plots of the catalysts recorded at an overpotential of 150 mV.
the practical applications. To illustrate the performance of the catalysts, the authors utilized a solar panel to power the water splitting process as depict in Figure 5b. When a 1.5 V solar panel is used, considerable hydrogen and oxygen bubbles are generated from the electrodes using the catalyst combinations of (II) (see Video II in the Supporting Information), (III) (see Video III) and (IV) (see Video IV) are utilized. On the contrary, few gas bubbles are produced from the combination of (I) (see Video I) owing to the slow reaction kinetics. When a 2.0 V solar panel was used, the generation of gas bubbles from the combination of (IV) becomes more intense (see Video V). Interestingly, the generation of gas bubbles is closely related to the intensity of the sunlight, which is attributed to the variations of current densities arisen from voltage fluctuations.

In summary, 3D core–shell structured NiFe-LDH@NiCu and NiFeOx@NiCu architectures were synthesized as bifunctional electrocatalysts for overall water splitting. The as-prepared NiFe-LDH@NiCu catalyst shows superior OER performance, resulting in an overpotential of 218 mV at a current density of 10 mA cm\(^{-2}\), which outperforms the precious RuO\(_2\) catalyst. The resulting NiFeO\(_x\)@NiCu possesses outstanding HER activity, leading to an overpotential of 66 mV at a current density of 10 mA cm\(^{-2}\), which is only slightly higher than that of precious Pt catalyst (53 mV). The excellent activity of the NiFe-LDH@NiCu and NiFeO\(_x\)@NiCu was demonstrated by a 1.5 V solar-panel-powered electrolyzer, yielding current densities of 10 and 50 mA cm\(^{-2}\) at overpotentials of 293 and 506 eV, respectively, which renders the as-prepared material as the second best bifunctional electrocatalyst so far. Such remarkable performance of the NiFe-LDH@NiCu and NiFeO\(_x\)@NiCu was attributed to the unique structures with abundant heterogeneous nanointerfaces, which not only afford the merits of the components, but also facilitate their synergistic effects in HER/OER processes. In addition, the assembly of ultrathin NiFe-LDH nanosheets or porous NiFe oxides onto the metallic NiCu core could afford large surface areas, fast electron transfer, facile access to electrolyte, and fast release of gas bubbles. This work could shed new insight on designing advanced electrocatalysts for water splitting.

**Experimental Section**

See the details in the Supporting information.

**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.

**Keywords**

hydrogen evolution reaction, layered double hydroxides and porous Ni–Fe oxides, oxygen evolution reaction, water splitting

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