A three-dimensional nickel–chromium layered double hydroxide micro/nanosheet array as an efficient and stable bifunctional electrocatalyst for overall water splitting†

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The development of bifunctional and stable non-noble metal electrocatalysts for the high-performance hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is very important and challenging for renewable energy. Herein, for the first time, a nickel–chromium layered double hydroxide (NiCr-LDH) nanosheet array was developed as a bifunctional electrocatalyst towards overall water splitting. By tuning different Ni/Cr ratios of LDHs, the optimized Ni2Cr1-LDH shows extraordinary HER activity with an ultralow overpotential of 138 mV at 100 mA cm\(^{-2}\), compared with all of the reported Ni-based LDHs (NiFe-LDH, NiCo-LDH, NiMn-LDH, NiTi-LDH, NiV-LDH etc.) and even outperforming Pt/C catalysts. The small overpotential of 319 mV at 100 mA cm\(^{-2}\) for the OER and outstanding durability at 1.55 V (vs. RHE) for 30 hours can also be achieved for Ni2Cr1-LDH. Notably, a two-electrode electrolyzer with a Ni2Cr1-LDH bifunctional electrocatalyst as both the anode and the cathode can work for at least 30 hours with a cell voltage of merely 1.55 V at 10 mA cm\(^{-2}\). Both experimental and density functional theoretical calculations show that the Cr\(^{3+}\) ions within the LDH layer serve as charge transfer sites and thus effectively boost the intrinsic electrochemical activity. Therefore, this work provides a new NiCr-LDH system as a more efficient metal hydroxide for bifunctional water splitting electrocatalyst.

Layered double hydroxide (LDH), also known as an anionic or hydratalcite-like clay, consists of layers of divalent and trivalent metal cations coordinated with hydroxide ions, accompanied by guest anion (CO\(_3^{2-}\), Cl\(^-\), etc.) intercalation between the layers. The two-dimensional (2D) layered structure endows the LDH systems with essential charge transport properties, which have been widely used in electrocatalysis. Particularly, benefitting from the Earth abundance and highly active OER activities, Ni-based LDHs (such as NiFe-LDH, NiCo-LDH, NiMn-LDH, NiFeMn-LDH, NiTi-LDH, NiV-LDH etc.) are considered as promising candidates. Furthermore, to enhance the electrochemical activities, several fabrication strategies have been developed. Firstly, to increase the number of active sites, hierarchical structures and micro/nanosheets have been constructed by the modification of the electrode. For example, due to the large porosity and good conductivity, many transition metal electrodes (such as nickel foam (NF)) have been selected as substrates. By direct growth of 2D LDH materials on these three-dimensional (3D) porous conductive substrates, highly active and stable electroactive catalysts can be designed. Secondly, the combination of both intrinsic electrochemical activity and high charge transfer of each catalytic site also became a major way. However, as is known, Ni or Co hydroxide is almost an insulator and causes...
poor charge transfer properties during the water splitting reaction.\textsuperscript{11,32} If the conductivity of the electrocatalysts can be increased, it will inevitably benefit the increase of reaction activity and reusability. From an elemental point of view, the Cr\textsuperscript{3+} cation presents a special electronic configuration (\textit{t}_{2g}^{1}\textit{e}_{g}^{0}\textit{g}), which facilitates charge transfer and electron capture.\textsuperscript{33} Thus, the incorporation of Cr\textsuperscript{3+} into Ni or Co hydroxide would be expected to increase the conductivity. As well, Cr\textsuperscript{3+} ions are easily oxidized to higher oxidation states during the OER, which in turn has a positive effect on the water oxidation active species (such as Co or Ni sites). For example, it has been reported that the addition of Cr\textsuperscript{3+} can increase the OER performance of Co-based LDH catalysts.\textsuperscript{34} Additionally, Jin and co-workers incorporated Cr into NiFe-LDH to improve the OER performance.\textsuperscript{35} However, whether Cr-containing LDHs could achieve high-efficiency electrocatalysis for both the OER and HER has not been investigated yet.

To develop new 2D efficient bifunctional electrocatalysts, in this work, we selected NiCr-LDHs as model systems, which have not been studied towards electrocatalytic overall water splitting before this work. A facile one-step hydrothermal method was developed to directly grow the 2D NiCr-LDH micro/nanosheet array onto 3D porous conductive NF, which could serve as a novel bifunctional catalyst for full water splitting for the first time. As a result, the developed Ni\textsubscript{x}Cr\textsubscript{y}-LDH electrode presents superior HER activity with ultralow overpotentials of 67 and 138 mV at 10 and 100 mA cm\textsuperscript{-2}, respectively, which are much lower than the values for majority of the reported Ni-based LDHs (such as NiFe-LDH,\textsuperscript{26} NiCo-LDH,\textsuperscript{20} NiMn-LDH,\textsuperscript{21} etc.). Moreover, the excellent OER activity of Ni\textsubscript{x}Cr\textsubscript{y}-LDH (an overpotential value of 319 mV at 100 mA cm\textsuperscript{-2}) could also be achieved. Notably, the two-electrode configuration cell with the Ni\textsubscript{x}Cr\textsubscript{y}-LDH electrocatalyst can work for a long period of time at a voltage of 1.55 V and deliver a current density of 10 mA cm\textsuperscript{-2}. Therefore, this work not only develops new types of NiCr-LDHs as bifunctional catalysts, but also provides new insight into the role of Cr\textsuperscript{3+} ions for promoting the electrochemical activities of the LDH layer.

Results and discussion

The NiCr-LDH samples with different Ni/Cr ratios (from 1 : 1 to 4 : 1) were prepared, in which the products are noted as Ni\textsubscript{x}Cr\textsubscript{y}-LDHs, where \textit{x} and \textit{y} stand for the relative feeding amount of Ni and Cr, respectively. XRD was firstly employed to confirm the structure of NiCr-LDH. As shown in Fig. 1, except for the peaks marked by pentacles belonging to NF, the diffraction peaks appear at 11.4°, 23.3°, 34.0°, and 60.8°, which can be assigned to the characteristic (003), (006), (009) and (110) facets of the LDH, respectively. These results strongly prove the successful fabrication of NiCr-LDH on the NF substrate.\textsuperscript{21,36} The interlayer spacing can be estimated as ca. 0.79 nm, corresponding to the CO\textsubscript{3}\textsuperscript{2–}–intercalated LDHs. Additionally, the relatively weak intensity and wider peak of (00l) diffractions indicate that the crystal degrees of LDHs are low, with thin 2D sheet-like structures.\textsuperscript{11}

Fig. 1 XRD patterns of Ni\textsubscript{2}Cr\textsubscript{1}-LDH, Ni\textsubscript{3}Cr\textsubscript{1}-LDH, Ni\textsubscript{4}Cr\textsubscript{1}-LDH and Ni\textsubscript{2}Cr\textsubscript{2}-LDH. The peaks marked by pentacle symbols are indexed to NF.

Next, the morphology of the Ni\textsubscript{2}Cr\textsubscript{2}-LDH samples was characterized by SEM. Numerous nanosheets with a size of ca. 100 nm and a thickness of ca. 20 nm were uniformly grown on the NF (Fig. 2a and S1–S4a, b†). The corresponding EDS analysis further discloses that the chemical compositions of Ni\textsubscript{2}Cr\textsubscript{2}-LDHs (Fig. S1–S4†) are consistent with the different feeding ratios. Furthermore, TEM images (Fig. 2b) confirm the nanosheet-like structure of Ni\textsubscript{2}Cr\textsubscript{2}-LDH. The high-resolution TEM image (inset in Fig. 2b) reveals that the interplanar spacing is 0.155 nm,\textsuperscript{17} which corresponds well with the \textit{d} spacing of the (110) plane of the typical LDH structure.\textsuperscript{11} The EDS mapping on the typical Ni\textsubscript{2}Cr\textsubscript{2}-LDH nanosheets verifies the homogeneous elemental distributions (Fig. 2c–g and Fig. S5†) of Ni, Cr, O and C compositions.

To study the surface chemical states of Ni\textsubscript{2}Cr\textsubscript{2}-LDH, XPS was further performed. As shown in Fig. 3a, two strong peaks of Ni 2p at 856.0 and 873.6 eV are assigned to the binding
energies of Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, indicating the existence of Ni(n) in Ni_{2}Cr_{1}-LDH. In the Cr 2p spectrum (Fig. 3b), two broad peaks located at 586.4 and 577.1 eV correspond to Cr 2P_{3/2} and Cr 2P_{1/2}, respectively. The peak at 577.7 eV is attributed to Cr^{3+} hydroxide, which also confirms that Cr ions are trivalent. The binding energy of Cr 2p at 577.7 and 576.5 eV suggests the formation of Cr–OH and Cr–O chemical bonds, respectively. The C 1s spectrum (Fig. 3c) at the main peak with a high binding energy at 289 eV corresponds to O–C=O in CO_{3}^{2−}, which demonstrates the presence of CO_{3}^{2−} intercalation in the LDH layer. Therefore, the XPS results confirm that the as-obtained NiCr-LDH nanosheets were stably grown on the NF.

The electrochemical HER performances for different NiCr-LDHs during water splitting were studied. All of the electrochemical measurements were applied in a standard three-electrode system with an electrolyte solution of 1.0 M KOH. The chemical measurements were applied in a standard three-electrode system with an electrolyte solution of 1.0 M KOH.

As a comparison, the bare NF and RuO_{2} were also tested under the same conditions. Ni_{4}Cr_{1}-LDH exhibits an overpotential of 136.9 mV at 100 mA cm\(^{-2}\). The electrocatalytic activity shows a similar trend to the HER. The polarization curves with iR compensation are shown in Fig. 4a. As a comparison, the bare NF and RuO\(_2\) were also tested under the same conditions. Ni_{4}Cr_{1}-LDH exhibits an overpotential of merely 138 mV. The comparison of Ni_{4}Cr_{1}-LDH reveals an overpotential of merely 138 mV. The excellent performance of the NiCr-LDH catalyst suggests the more effective mass transport and faster reaction kinetics in the HER. Such performance is also comparable to the recently reported HER electrocatalysts such as Ni@NC (≈300 mV at 100 mA cm\(^{-2}\)),\(^{42}\) Co_{3}Ni_{2}P NTs (≈490 mV at 100 mA cm\(^{-2}\)),\(^{43}\) NiCo_{2}S_{4} (≈350 mV and 245 mV at 100 mA cm\(^{-2}\)),\(^{27}\) Ni_{2}P_{4} (≈323 mV at 100 mA cm\(^{-2}\)),\(^{34}\) VOOH (≈270 mV at 100 mA cm\(^{-2}\)),\(^{44}\) porous NiFe/NiCo_{2}O_{4}/NF (200 mV at 100 mA cm\(^{-2}\)),\(^{28}\) NiFeO_{x}/CFP (≈230 mV at 100 mA cm\(^{-2}\)),\(^{46}\) and Ni_{3}S_{2}/NF (≈400 mV at 100 mA cm\(^{-2}\)).\(^{47}\) Furthermore, the Tafel slope of Ni_{2}Cr_{1}-LDH is 61.5 mV dec\(^{-1}\), which is much lower than that of Ni_{1}Cr_{1}-LDH (72.2 mV dec\(^{-1}\)), Ni_{3}Cr_{1}-LDH (62.2 mV dec\(^{-1}\)), Ni_{3}Cr_{1}-LDH (80.1 mV dec\(^{-1}\)), bare NF (136.9 mV dec\(^{-1}\)) and even Pt/C (64.2 mV dec\(^{-1}\)), as shown in Fig. 4b. The long-term durability of the catalyst is also a critical parameter, and thus we further carried out a durability test of the Ni_{3}Cr_{1}-LDH electrode. The I–t curve (Fig. 4c) shows that the catalytic current density exhibits a numerical retention after 30 h of continuous measurement under a constant potential of −0.07 V versus RHE, suggesting its outstanding durability.

For the OER process on Ni_{3}Cr_{1}-LDH electrodes, the electrocatalytic activity shows a similar trend to the HER. The polarization curves with iR compensation are shown in Fig. 5a. The oxidation peak at about 1.4 V for all NiCr-LDHs is due to the oxidation state of Ni from bivalent to trivalent to form NiOOH.\(^{27,48,49}\) It has been confirmed that in the OER process, the catalytically active site of the Ni-based catalyst is located in the structure of NiOOH, which plays a vital role in the OER activity.\(^{50}\) The bare NF shows poor OER properties, while RuO\(_2\) presents a large overpotential of 420 mV at 50 mA cm\(^{-2}\). In contrast, Ni_{3}Cr_{1}-LDH exhibits the preferable OER performance.
in terms of the overpotential of 364 mV at 100 mA cm$^{-2}$. The increased activity of Ni$_1$Cr$_1$-LDH, Ni$_2$Cr$_1$-LDH and Ni$_3$Cr$_1$-LDH can be observed apparently from the negative shift of the LSV curve. It is worth noting that the Ni/ Cr ratio of 2 : 1 achieves the highest OER activity in terms of the lowest overpotentials of 319 mV and 390 mV at 100 and 300 mA cm$^{-2}$, respectively. Remarkably, the $\eta_{100}$ value for Ni$_2$Cr$_1$-LDH is comparable to those of other state-of-the-art OER catalysts, such as NiCo$_2$O$_4$, FeNi@single layer graphene, VOOH$_4$ and CoMnCH$_2$ (Table S2$^\dagger$), and is much smaller than those of the reported systems for Ni-based LDHs (460 mV$^\ddagger$, $\approx$320 mV$^\dagger$, $\approx$420 mV (ref. 20) and 349 mV (ref. 25) at 100 mA cm$^{-2}$). Such good performance can be related to the orientational growth of 2D LDH nanosheets onto the 3D networks, which not only provides a large surface area, but also exposes more accessible active sites contributing to high current densities. Fig. 5b presents the Tafel plots derived from the corresponding LSV curves. The bare NF and RuO$_2$ deliver the Tafel slope of 121.3 mV dec$^{-1}$, while Ni$_2$Cr$_1$-LDH shows the lowest Tafel slope of 22.9 mV dec$^{-1}$, suggesting that Ni$_2$Cr$_1$-LDH has favorable kinetics of electrochemical water oxidation. Furthermore, the stability was tested under a constant potential of 1.55 V versus RHE for 30 hours, and the catalytic current density displays even a slight increase, implying the high stability of the NiCr-LDH catalyst after OER catalysis. Fig. S7$^\dagger$ shows the Ni 2p and Cr 2p XPS spectra of the post-OER Ni$_2$Cr$_1$-LDH sample. As shown in Fig. S7$a$, the Ni 2p XPS spectrum shows a new signal for NiOOH, which is located at 857.9 eV after OER catalysis. Moreover, XPS spectroscopy of Cr species indicates that there is no additional peak after OER measurement (Fig. S7$b$). Since the oxidation of Ni changes the local chemical environment, Cr 2p is slightly shifted to a higher binding energy. This slight change in the surface valence state is consistent with the high stability of the Ni$_2$Cr$_1$-LDH electrode.

The above experiments show that the overpotentials of both the HER and OER are the lowest when the Ni/ Cr ratio in NiCr-LDH is 2 to 1. To better understand the factors influencing the highly enhanced catalytic activity of Ni$_2$Cr$_1$-LDH relative to other electrodes, the electrochemically active surface areas (ECSA) of NiCr-LDH with different Ni/Cr ratios were evaluated by measuring the double-layer capacitances ($C_{dl}$) through collecting CV in a non-faradaic potential range of 1.05−1.15 V vs. RHE at different scan rates (Fig. S8$a$–$d$). The ECSA values of Ni$_2$Cr$_1$-LDH are 22.9 mF cm$^{-2}$, which is about 2.1 times, 1.4 times and 3.3 times higher than those of Ni$_1$Cr$_1$-LDH (10.8 mF cm$^{-2}$), Ni$_3$Cr$_1$-LDH (16.3 mF cm$^{-2}$) and Ni$_4$Cr$_1$-LDH (6.9 mF cm$^{-2}$), respectively. The current density of the NiCr-LDH samples can be normalized to their corresponding ECSAs for a reasonable comparison. The higher ECSA of Ni$_2$Cr$_1$-LDH reveals that it has the largest effective surface area. Obviously, NiCr-LDH with the highest ECSA value of 2 : 1 exhibits the best HER and OER activities. Turnover frequency (TOF) is also a key kinetic parameter for the OER, indicating the intrinsic properties of the electrocatalytic activity. Here, it is assumed that all metal sites in NiCr-LDH are electrochemically active in the water oxidation reaction, and their turnover frequencies at an overpotential of 400 mV can be calculated. Ni$_3$Cr$_1$-LDH shows a much higher TOF (0.119 s$^{-1}$), which is approximately 1.1, 1.3, and 1.6 times higher than the corresponding values for Ni$_1$Cr$_1$-LDH (0.112 s$^{-1}$), Ni$_3$Cr$_1$-LDH (0.091 s$^{-1}$), and Ni$_4$Cr$_1$-LDH (0.073 s$^{-1}$), respectively. It is worth mentioning that the above-mentioned TOFs are obviously underestimated because some metal sites may be electrochemically inaccessible.

To confirm the role of Cr$^{3+}$ in the excellent HER and OER activities of NiCr-LDH, Ni(OH)$_2$ and Cr(OH)$_3$ were also prepared and compared with NiCr-LDH under the same experimental conditions (Fig. S9$^\dagger$). We also investigated the HER and OER activities of Ni(OH)$_2$ and Cr(OH)$_3$ onto the NF electrode. As shown in Fig. S10$a$, the current density of Ni$_3$Cr$_1$-LDH at −0.1 V (vs. RHE) is 27.8 mA cm$^{-2}$ for the HER, which is 6.8 times larger than that of Ni(OH)$_2$ (4.1 mA cm$^{-2}$) and 55.6 times larger than that of Cr(OH)$_3$ (0.5 mA cm$^{-2}$). Meanwhile, the current density of Ni$_3$Cr$_1$-LDH at 1.6 V (vs. RHE) is 208.6 mA cm$^{-2}$ for the OER, which is 11.3 times larger than that of Ni(OH)$_2$ (18.4 mA cm$^{-2}$) and 29.4 times larger than that of Cr(OH)$_3$ (7.1 mA cm$^{-2}$) as shown in Fig. S10$b$. Moreover, the capacitance values of Ni$_3$Cr$_1$-LDH, Ni(OH)$_2$ and Cr(OH)$_3$ are 22.9 mF cm$^{-2}$, 1.8 mF cm$^{-2}$ and 1.1 mF cm$^{-2}$,
respectively (Fig. S11†), suggesting that NiCr-LDH has the highest electrochemical surface area. More importantly, the conductivity of Ni2Cr1-LDH, Ni(OH)2 and Cr(OH)3 was evaluated by electrochemical impedance spectroscopy (EIS). The Nyquist plots of the three electrodes show a significant semicircle in the high frequency range that can be correlated with the charge transfer resistance (Rct) of the LDH catalysts. Fig. S12† shows that Ni2Cr1-LDH possesses the smallest Rct (0.51 Ω) in contrast to that for Ni(OH)2 (7.04 Ω) and Cr(OH)3 (12.09 Ω), suggesting that the doping of Cr3+ can increase the intrinsic conductivity and the electron transfer efficiency, and thus further improve the catalytic performance of the OER. These results clearly demonstrate that NiCr-LDH exhibits superior performance relative to the pristine Ni(OH)2 and Cr(OH)3.

Díaz-Morales et al. believe that the catalytically active site of NiCr-LDH is considered to be the Ni ion rather than the Cr site.53 It is well known that nickel hydroxide is almost an insulator, which results in poor reactivity due to poor charge transfer properties in the reaction.54 If the conductivity of the material is increased, the electrochemical activity will inevitably increase. In order to detect the role of Cr3+ in the LDH layer, periodic density functional theoretical (PDFT) calculations were performed on idealized models of Ni2Cr1-LDH.55 The calculated band gap is ca. 0.178 eV, suggesting the highly conductive properties. The total and partial electronic densities of state (TDOS and PDOS, respectively, Fig. 6 and Fig. S13†) show that the top of the valence band (TVB) of NiCr-LDH is populated with both Cr and Ni electrons, while the bottom of the conducting band (CB) is mainly contributed by the 3d atomic orbitals of Cr, suggesting the potential electronic transfer between Ni(OH)2 and adjacent Cr(OH)3, as well as the strong electron conductivity in the NiCr-LDH layer. The PDOS profiles of majority spin and minority spin for both Ni and Cr metals present an unsymmetrical distribution, which indicates that the electron spin-polarization between Ni2+ and Cr3+ may also play an important role in the electronic transport, which is consistent with NiCr-LDH that presents a high electrocatalytic activity during the OER and HER in experiment. Additionally, the calculated models for Ni3Cr1-LDH and Ni3Cr1-LDH were further analyzed (Fig. S14 and S15†), in which the TDOS/PDOS and the band gap are very similar to those of Ni3Cr1-LDH.

In view of the excellent OER and HER performances of bifunctional NiCr-LDH, the overall splitting of water was tested in a two-electrode configuration cell (Video S1†). It is observed that the Ni3Cr1-LDH bifunctional electrocatalyst requires a cell voltage of merely 1.55 V to deliver a current density of 10 mA cm−2 (Fig. 7). Such a low overpotential of the LDH electrocatalyst for overall water splitting is impressive and comparable to the lowest values for the recently reported overall water splitting materials including NiFe-LDH (1.7 V at 10 mA cm−2),26 CoMnCH (1.68 V at 10 mA cm−2),25 Ni3P4 (1.7 V at 10 mA cm−2),44 VOOH (1.62 V at 10 mA cm−2),45 NiSe/NF (1.63 V at 10 mA cm−2)56 and CoP (1.62 V at 10 mA cm−2)57 (Table S3†). More worth emphasizing is that the Ni3Cr1-LDH//Ni3Cr1-LDH electrocatalyst of the two-electrode configuration shows much higher durability after 30 hour long-term measurement. The morphology and the corresponding EDS mapping images of Ni3Cr1-LDH after the durability test were also collected (Fig. S16†). Even in the case of a long durability test, it is obvious that the nanosheet array structure is maintained very well, consistent with its stable water splitting performance. The EDS mapping results also suggest the homogeneous distribution of Ni, Cr, O, and C elements. These results promise Ni3Cr1-LDH as a new type of electrocatalyst for practical overall water splitting in alkaline media.

Based on both experiment and theoretical calculations, in our opinion, the high OER/HER performance and good stability of NiCr-LDH can be attributed to the following points: (i) the 3D porous structure closely organizes the hierarchical 2D active nanosheets, which could expose more active sites, and facilitate charge transport and gas release in the hierarchical architecture; (ii) the synergistic effect of redox-active cations (Ni and Cr) and Lewis-acid cations (Cr) could enhance the elec-
troncic interaction in the metal hydroxide matrix, and have a positive effect on the activity of electrocatalytic reactions: redox active cations (Ni3+/Ni4+) with a high oxidation state are believed to be potentially active sites in the NiCr-LDH OER catalyst. The addition of Cr3+ cations with a trivalent oxidation state can also buffer the multi-electron processes required for water oxidation. In the LDH layer, the metal cations are bonded to each other through bridged hydroxyl bonds. Cr3+ as Lewis acid cations can modulate the ligand fields of these hydroxyl groups; (iii) the Cr3+ cation presents a unique electronic configuration (t2ge0g), which facilitates charge transfer, conductivity and electron capture. Different from the previously studied Ni-based LDHs, such as NiFe-, NiCo-, NiMn-, NiTi-, and NiV-LDH, this work demonstrates the improved intrinsic activity of the electrocatalysts by designing the suitable catalyst composition (Cr3+ cation) and the effect of high-active-area nanostructures with optimized open frameworks on the overall water splitting performance.

Conclusions

In summary, new types of 2D NiCr-LDH nanosheet arrays with 3D porous microstructures were synthesized through a simple and one-step hydrothermal method, which were further used as bifunctional catalysts towards the overall water splitting. The NiCr-LDHs serve as efficient and stable bifunctional catalysts for electrocatalytic water oxidation and reduction, in which the optimized NiCr-LDH shows an ultralow overpotential of 67 mV at 10 mA cm⁻² for the HER, 319 mV at 100 mA cm⁻² for the OER and excellent long-term durability in alkaline media, which is superior to the most current Ni-based LDH electrocatalysts. The combination of experiments and DFT calculations provides a basic understanding of their electronic structures and spin-polarization, confirming the role of Cr-based LDH in the high electron conductivity for the HER and OER processes. Furthermore, a two-electrode configuration cell using NiCr-LDH as both the anode and cathode indicated a practical setup for efficient and stable overall water splitting with a cell voltage of merely 1.55 V to deliver a current density of 10 mA cm⁻². It can be expected that the NiCr-LDH nanosheet based electrocatalysts with high activity and stability have potential application prospects in large-scale electrochemical water splitting.

Experimental section

Materials

Ni(NO₃)₂·H₂O, Cr(NO₃)₃·9H₂O and urea were purchased from Macklin. All reagents were of analytical grade and were used without further purification. Deionized water was used throughout the experiments. Ni foam (NF) was used as a substrate. The NF needs to be pretreated to remove the surface oxidation layer. Firstly, the NF was washed in an ultrasonic bath of acetone for 10 min. Subsequently, it was soaked in HCl solution (3 M) for 3 min, and then rinsed with deionized water and ethanol 3 times, respectively.

Synthesis of NiCr-LDH/NF

NiCr-LDHs on NF were synthesized by a one-step hydrothermal reaction. Typically, Ni(NO₃)₂·H₂O (0.6 mmol) and Cr(NO₃)₃·9H₂O with different ratios (1:1, 2:1, 3:1 and 4:1) and urea (2 mmol) were dissolved in 15 mL of deionized water to form a homogeneous solution, then transferred into a 23 mL Teflon-lined stainless-steel autoclave containing a piece of cleaned NF (1 cm × 2 cm) and then hydrothermally treated at 120 °C for 12 h. Finally, the autoclave was cooled down to room temperature. The resulting brownish green sample on NF was washed with ethanol and dried naturally in air overnight. The mass loading of final NiCr-LDH products on the NF was about 2 mg cm⁻².

Synthesis of Ni(OH)₂/NF and Cr(OH)₃/NF

Ni(OH)₂ on Ni foam were produced by a hydrothermal method according to a previous report. The synthesis of Cr(OH)₃ was similar to that of Ni(OH)₂.

Fabrication of RuO₂ and Pt/C on Ni foam

5 mg of RuO₂ or Pt/C powder was dispersed in 50 μL of 5 wt% Nafion and 250 μL of ethanol followed by sonication for 30 min. Then, 10 μL of the catalyst ink was loaded on Ni foam (1 cm × 2 cm) and dried at 70 °C for 1 hour.

Characterization

Powder X-ray diffraction (XRD) patterns of all the samples were obtained using graphite-filtered Cu Kα radiation operating at 40 kV and 30 mA, λ = 0.15418 nm (Shimadzu XRD-6000 diffractometer). Scanning electron microscopy (SEM) with an accelerating voltage of 20 kV (SEM, Zeiss SUPRA 55) was applied for detailed morphology analyses. X-ray photoelectron spectrometry (XPS) was performed using Al Kα radiation (Thermo VG ESCALAB MK II). The positions of all BEs were calibrated using the C 1s line at 284.8 eV. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) mappings were obtained using microscopy (JEOL JEM-2010F) combined with EDX (Oxford X-MaxN 80-TLE) spectroscopy. For TEM evaluation, the samples were scraped from the Ni foam substrate and ultrasonically dispersed in ethanol and then a drop of the suspension was deposited onto a carbon-coated Cu grid followed by the evaporation of solvent in air.

Electrochemical measurements

Electrochemical measurements were conducted on a CHI 660E electrochemical workstation (CH Instruments Co. USA) with an electrolyte solution of 1.0 M KOH (the electrolyte was degassed by bubbling nitrogen for 30 min), using a standard three-electrode system with NiCr-LDH/NF (1 cm × 1 cm) as the working electrode, a Pt wire (2 cm) as the counter electrode and an Ag/AgCl electrode as the reference electrode.
Commercial Pt/C and RuO₂ were used as references for comparing the electrocatalytic performance of various samples. All potentials measured in this work were referenced to the reversible hydrogen electrode (RHE) scale on the basis of the Nernst equation: \( E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059 \, \text{pH} \). Linear sweep voltammetry (LSV) was performed at 5 mV s\(^{-1}\) to obtain the polarization curves and Tafel plots. The stability test was performed using chronopotentiometric measurements. The electrochemical surface area (ECSA) was measured using cyclic voltammetry (CV) in a non-faradaic potential range at various scan rates including 10, 20, 30, 40, 60, and 80 mV s\(^{-1}\). The super-αmeters: \( R \), the space group of the LDHs is \( \text{R}3m \), with unit cell parameters: \( \alpha = \beta = 90°, \gamma = 120° \). The supercell of the octahedral layer has 12 metal atoms and 24 OH groups and the distance between the adjacent metal atoms is 3.05 Å. The ratio of Ni/Cr is 2:1, which is similar to the experimental result. The supercell is \( 4 \times 3 \times 1 \) in the \( a \), \( b \), and \( c \)-direction, and two CO\(_3\)\(^{2-}\) are localized on LDH in each model. All calculations were performed with the periodic density functional theory (DFT) method using the CASTEP module in the Material Studio software package.\(^{58}\) The configurations were optimized at the generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) level.\(^{59}\)

**Structural model and DFT calculation**

The space group of the LDHs is \( \text{R}3m \), with unit cell parameters: \( \alpha = \beta = 90°, \gamma = 120° \). The supercell of the octahedral layer has 12 metal atoms and 24 OH groups and the distance between the adjacent metal atoms is 3.05 Å. The ratio of Ni/Cr is 2:1, which is similar to the experimental result. The supercell is \( 4 \times 3 \times 1 \) in the \( a \)-, \( b \)- and \( c \)-direction, and two CO\(_3\)\(^{2-}\) are localized on LDH in each model. All calculations were performed with the periodic density functional theory (DFT) method using the CASTEP module in the Material Studio software package.\(^{58}\) The configurations were optimized at the generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) level.\(^{59}\)

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**
