

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Towards superior oxygen evolution through graphene barriers between metal substrates and hydroxide catalysts

Hao-Fan Wang, Cheng Tang, and Qiang Zhang^{*,†}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Oxygen evolution reaction (OER) plays a key role in various sustainable energy systems, such as solar cells, fuel cells and metal-air batteries. The wise integration of transition metal compounds with macroscale current collector is a promising strategy to achieve OER catalysts with a high utilization efficiency. Herein, graphene with superior electron pathway, high surface area, conductive mechanical properties, and conjugate plane to anchor other phases with good dispersion was employed as the barrier between 3D Ni foam and NiFe-LDHs for 3D monolith electrode. The as-obtained electrode exhibited a remarkably low onset overpotential of 240 mV, a small overpotential of 325 mV for 10 mA cm⁻² and a substantially decreased Tafel slope of 44 mV dec⁻¹ in 0.1 M KOH. The graphene barrier herein not only provides a novel hydrophobic substrate to modulate the growth of 3D NiFe LDHs with good dispersion, but also delivers a strongly coupled interface between active phase and current collectors. Consequently, the as-obtained graphene mediated 3D monolith electrode was with a very high electrochemical active surface area, an optimal interfacial junction, as well as superior OER performance. This work provides a novel catalyst for OER and more importantly, it reveals the role of graphene to modulate the interfacial features of various composites, which is general and can be employed in many material systems for satisfactory applications in heterogeneous catalysis, energy conversion and storage, sensors and so on.

1. Introduction

The energy systems based on fossil fuels and biomass, which is the lifeblood of modern society originally come from solar energy, captured and transformed through photosynthesis. However, the low photosynthetic efficiency and sluggish transformation process lead to a gradual diminution of fossil fuels, and the resultant CO₂ emissions are regarded as the main factor towards climate change. Consequently, an alternative and sustainable energy system is urgent to be developed to meet the requirements of today's society. Artificially converting water and carbon dioxide into oxygen and organics is of great promise for mitigating the energy crisis, and enhancing the material circulation in the global ecosystem. The oxygen evolution reaction (OER, 4OH⁻ → O₂ + 2H₂O + 4e⁻ in alkaline solution, with an equilibrium potential of 1.23 V vs. reversible hydrogen electrode, RHE) is demonstrated to play a key role in this energy cycle, while suffers from sluggish kinetics and high overpotentials.¹

To make the OER process more efficient for practical applications, various kinds of catalysts have been designed and applied into this reaction. Noble metal and their oxides are commonly acknowledged as the most high-efficient OER electrocatalysts,² but their applications are hindered by the high cost and poor durability. Recently, non-precious metal and their compounds (Fe, Co, Ni, Mn, etc.),³⁻¹² the OER activity of which are demonstrated to be rival to noble metal oxides such as RuO₂ and IrO₂¹³ on computational volcano curves, have attracted great attentions as a family of promising alternatives. Among them, layered double hydroxides (LDHs),³⁻⁷ especially NiFe and NiCo LDHs,^{3-6, 10} are widely investigated and recognized as the most highly active catalysts for OER. In these works, the catalysts were generally dropped onto the working electrode, and adhered to it by the aid of binders. It's notable that the catalysts will easily flake off due to the oxygen bubbles generating and escaping from the surface constantly during OER process, thereby resulting in a low durability and unstable performance. Aiming at this problem, some recent works employed Ni foam as a three-dimensional (3D) porous and conductive substrate.^{6, 11} Via *in situ* nucleation and growth, hierarchical LDH sheets were grown from and anchored onto the Ni substrate to serve as freestanding working electrodes directly.

In spite of a 3D hierarchical structure and binder-free preparation, the poorly conductive LDH sheets packed and banked on the Ni substrate surface, which resulted in a limited

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China. E-mail: zhang-qiang@mails.tsinghua.edu.cn

[†] H.F. Wang and C. Tang contribute equally.

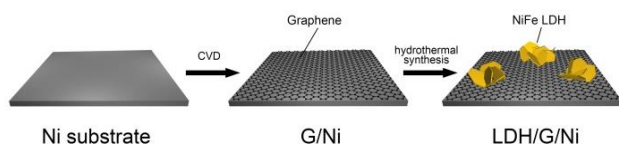
Electronic Supplementary Information (ESI) available: SEM images, TEM images, EDS pattern, TGA plots, and chronoamperometric response of LDH based catalyst, the morphology evolution of G/Ni during the OER process, and a summary of the OER performances of on transition metal compounds based catalysts. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/x0xx00000x

ARTICLE

electron transportation through the catalytic phase and an insufficient utilization of the active sites. Consequently, the fine arrangement of LDH sheets on Ni substrates and the interfacial modulation still remain a challenge towards a high efficiency and full demonstration of LDH/Ni systems for OER electrocatalysis.

In this contribution, an ultrathin graphene layer was introduced to modulate the growth behaviors and catalytic performances of NiFe LDHs on the Ni foam substrate (denoted as LDH/G/Ni), as illustrated in Scheme 1. The incorporation of graphene with a high surface area and excellent performance on electron transport is believed to be an effective solution to enhancing the electrical conductivity and dispersion of LDHs.^{3, 12, 14} Besides, the graphene layer served as a barrier between Ni substrate and the precursor solution of LDHs, which appropriately suppressed the subsequent growth of LDH sheets. Moreover, the atom-thick layer of graphene still retained an adequately strong interaction between LDHs and the Ni substrate, and the rich valence states of Ni (Ni^0 , Ni^{2+} , Ni^{3+}) are believed to contribute to a low OER onset potential¹⁵. Consequently, the novel LDH/G/Ni complex was demonstrated to exhibit an excellent OER performance with a low onset overpotential of 240 mV and a greatly decreased Tafel slope of 44 mV dec^{-1} .



Scheme 1. Synthesis of LDH/G/Ni electrocatalysts with graphene barrier between Ni substrates and layered NiFe hydroxides.

2. Results and discussion

Structure of graphene barrier mediated OER catalyst

To obtain this hybrid material, a continuous layer of graphene was firstly grown on Ni foam by a chemical vapor deposition (CVD) method in advance¹⁶ and then NiFe LDHs were fabricated on the graphene by a hydrothermal co-deposition method (Scheme 1). The nickel and iron nitrate were fed into the hydrothermal reactor at a mole ratio of 3:1. Methanol was utilized as the alkali source instead of common urea to mitigate the corrosion of the Ni foam and surfactant cetyltrimethyl ammonium bromide (CTAB) was introduced to obtain more uniform LDH sheets.¹⁷ Meanwhile, the complex of NiFe LDHs and Ni foam without graphene (LDH/Ni) was also synthesized under otherwise identical conditions. As the low magnification scanning electron microscopy (SEM) image of G/Ni shown in Fig. 1a, a continuous thin layer of graphene was observed to attach on the Ni foam. After LDH growth, the Ni framework remained its structural integrity without any crush or corrosion, and uniform LDHs were decorated on the graphene above Ni substrate (Fig. 1b). Notably, with the LDH growth proceeded, interspersed LDH seeds firstly nucleated all over the surface of graphene in G/Ni, and then gradually grew

to small LDH clusters as shown in Fig. 1c, while in the case of LDH/Ni, swarms of LDHs quickly generated on the surface of Ni resulting to continuously cover the substrate (Fig. S1). This distinct nucleation and growth behaviour was rationalized by the introduction of hydrophobic, low-defective graphene layers, which increased the LDH nucleation resistance, as well as prevented Ni foam to dissolve and serve as the nickel source of LDHs, thus moderately suppressed the LDH nucleation and the vertical growth of LDH sheets. The impact of the graphene hydrophobicity was furtherly supported by the different morphologies of LDHs fabricated on graphene substrates with a hydrophobicity gradient (Fig. S2). This loose arrangement of LDHs ensured free space for oxygen transport, electrolyte penetration, and easily accessible active sites; meanwhile, the underlayer graphene linked up all the separated LDH sheets with an interconnected electron pathway.

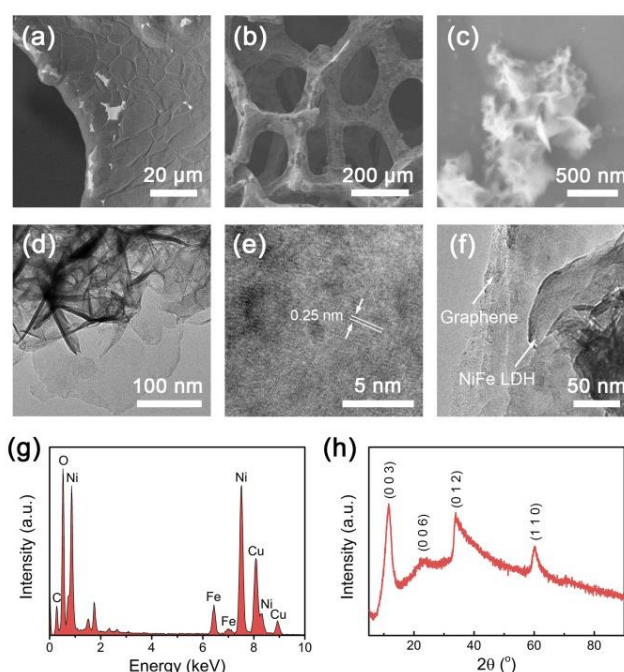


Fig. 1. The characterization of the LDH/G/Ni electrocatalysts. (a) SEM image of G/Ni. (b, c) SEM images of LDH/G/Ni, showing the interspersed LDH sheets on G/Ni. (d, e) TEM images of the NiFe LDHs from LDH/G/Ni electrocatalysts. (f) TEM image of NiFe LDHs and graphene. (g) EDS pattern of NiFe LDHs. (h) XRD pattern of p-LDH.

The as-grown LDH sheets were so thin that nearly transparent under transmission electron microscopy (TEM, Fig. 1d) with a fringe spacing of 0.25 nm in accordance with the (012) lattice plane of NiFe LDHs (Fig. 1e), and interconnected to form flower-like clusters as shown in SEM (Fig. 1c). Graphene could also be detected by TEM (Fig. 1f), accompanied with LDH sheets. The TEM sample was prepared by ultrasonic method. Even after a strong ultrasonic treatment for 60 min at a high power (300 W, 40 kHz), the LDH/G/Ni block exhibited no significant change, and only several clusters of LDH and graphene could be observed on the micro grid. This phenomenon indicated the strong couple interaction between NiFe LDHs and Ni substrate with a thin graphene layer in-

between. The elemental composition of the LDH sheets in Fig. 1d were measured by energy dispersive spectrometer (EDS, Fig. 1g) with a mole ratio of Ni/Fe to be 6.0:1, much higher than that of the feedstock, which was probably due to the slight dissolution and Ni supply from the Ni foam. For further study of the LDH crystal structure, X-ray diffraction (XRD) test was performed. However, the as-grown NiFe LDHs were difficult to separate from Ni foam, so the LDH precipitate (p-LDH) in the hydrothermal reactor was utilized as the substitute for XRD test. The TEM image and EDS pattern revealed that p-LDH exhibited a similar morphology and composition with LDH grown on Ni foam (Fig. S3). The XRD pattern (Fig. 1h) of p-LDH showed obvious peaks at $2\theta = 11.4^\circ$, 23.0° , 34.4° , and 60.0° , representing the (003), (006), (012), and (110) planes of the NiFe LDH crystal. The above results indicated the successful fabrication of a LDH/G/Ni hybrid with graphene incorporation to regulate the growth behaviors and interfacial interaction of LDH and Ni substrate.

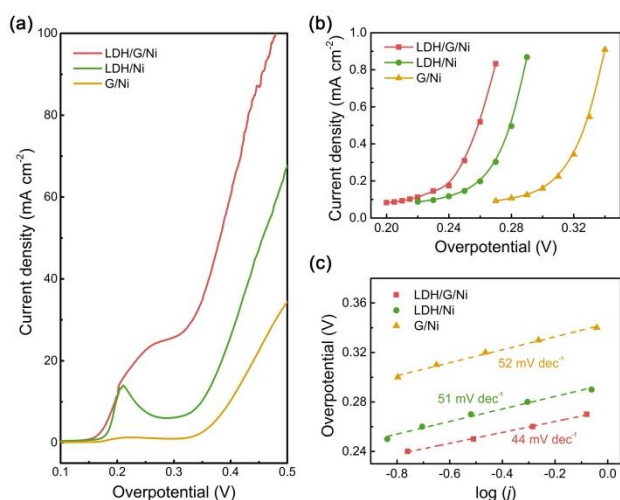


Fig. 2. The OER performances of LDH/G/Ni electrocatalysts. (a) i-R compensated LSV curves. The scan rate was 10 mV s^{-1} . (b) Voltammetric curves obtained by chronoamperometric method. (c) Tafel plots. All the measurements were performed in O_2 saturated 0.1 M KOH solution.

OER electrocatalytic performance

To investigate the OER catalytic activity of LDH/G/Ni, it was employed as the working electrode in a three electrode system. Owing to the stable 3D structure of the Ni foam and the conductive scaffold, no binder or additional substrate was required. All electrochemical experiments were performed in 0.1 M KOH solution in comparison with LDH/Ni and G/Ni. The linear sweep voltammetry (LSV) plots at a scan rate of 10 mV s^{-1} were presented in Fig. 2a. The values of the OER current density are directly associated with the reaction process and thereby the catalyst activities. With the highest current density, LDH/G/Ni exhibited a superior performance to the contrast samples. The rise of the current at the overpotential around 0.2 V is assigned to the oxidation current of Ni, and for those samples containing LDH, it also includes the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox

current. In the LSV test of G/Ni, the silver foam turned black at high overpotential (Fig. S4), indicating the generation of nickel hydroxides, which was demonstrated to be active for OER catalysis.¹⁸ Additionally, the NiOOH phase generated by the $\text{Ni}^{2+}/\text{Ni}^{3+}$ transformation is believed to be crucial to the working active sites of LDH during OER process.⁹ Hence, these two oxidation processes, as represented by the redox peak around 0.2 V , were expected to bring about an enhancement to the OER activity, which was supported by the fact that the higher the redox current, the better the OER performance for LDH/G/Ni.

It is noteworthy that in the LSV plot of LDH/G/Ni, the potential ranges for catalyst oxidation and oxygen evolution are partly overlapped, which makes it quite difficult and system-specific to determine the accurate onset potential and Tafel slope as well. To decouple these two reactions, a chronoamperometric testing method was devised to obtain sole OER current densities at specific overpotentials (see Supporting Information for details). With this method, the onset overpotentials (η_{onset}) of LDH/G/Ni, LDH/Ni, and G/Ni were determined to be 0.24 , 0.25 , and 0.30 V (Fig. 2b). Fig. 2c exhibited the Tafel plots derived from the data in Fig. 2b. LDH/G/Ni also delivered the smallest Tafel slope (44 mV dec^{-1}), while the Tafel slopes for LDH/Ni and G/Ni were 51 and 52 mV dec^{-1} , respectively. The small Tafel slope of LDH/G/Ni indicated a lower electrochemical polarization. Besides the onset overpotential and Tafel slope, the overpotential required to reach a current density of 10 mA cm^{-2} (η_{10}) and the current density at $\eta = 350 \text{ mV}$ (j_{350}), which are related to the promising OER application in a solar water splitting device¹⁹ are also two important parameters. As summarized in Table 1, the LDH/G/Ni composite exhibited undoubtedly best performances compared with other samples, and also among the best results in recent reports (Table S1).

Table 1. Summary of the OER performances of LDH/G/Ni, LDH/Ni and G/Ni.

Samples	η_{onset} (mV)	η_{10} ^{a)} (mV)	j_{350} (mA cm^{-2})	Tafel slope (mV dec^{-1})
LDH/G/Ni	240	325	34.8	44
LDH/Ni	250	350	10.3	51
G/Ni	300	399	2.6	52

^{a)} The η_{10} for LDH/G/Ni and LDH/Ni can't be obtained from the LSV plots. Just like the onset potential, η_{10} was measured by chronoamperometric method as discussed in the Supporting Information.

The relationship between the 3D structure and OER activity

The efficient catalysts for OER require not only sufficient active sites, but also a specific hierarchical structure as well as a strongly coupled interface between supports and active sites. Taken the different structural features into consideration, it is rational to conclude that in addition to the intrinsic catalytic activity of NiFe LDHs and the 3D scaffold of Ni foam, the introduction of graphene tunes the interfacial characters of LDH/Ni with a more active state and an enhanced electron

transfer, thereby boosting up the OER activity. Detailed discussion is conducted to elucidate the relationship between structure and function for LDH/G/Ni catalyst.

On one hand, the NiFe LDH sheets, as active phases for OER, possess some beneficial structural features to this process. LDH is a kind of anion intercalated hydroxide, thus presents excellent hydrophilicity. Fig. 3a shows the contact angle tests of LDH/G/Ni and G/Ni tableting samples using deionized water as the wetting liquid. With the introduction of LDHs, the contact angle was greatly decreased from 103.0° to 60.4°, demonstrating a remarkably improved surface wettability and thereby an enhanced electrolyte permeation and affinity. It was further confirmed by the measurement of the electrochemically active surface area (ECSA). Fig. 3b described the plots of double-layer capacitance (C_{dl}) test. The slope of each fitting line, equal to twice the C_{dl} of corresponding material, is proportional to the ECSA.¹⁹ Notably, besides G/Ni, the ECSA of LDH/G/Ni was also higher than that of LDH/Ni, which suggested that the hydrophobic but highly conductive graphene layer improved the interfacial interaction and electrocatalysis during OER process.

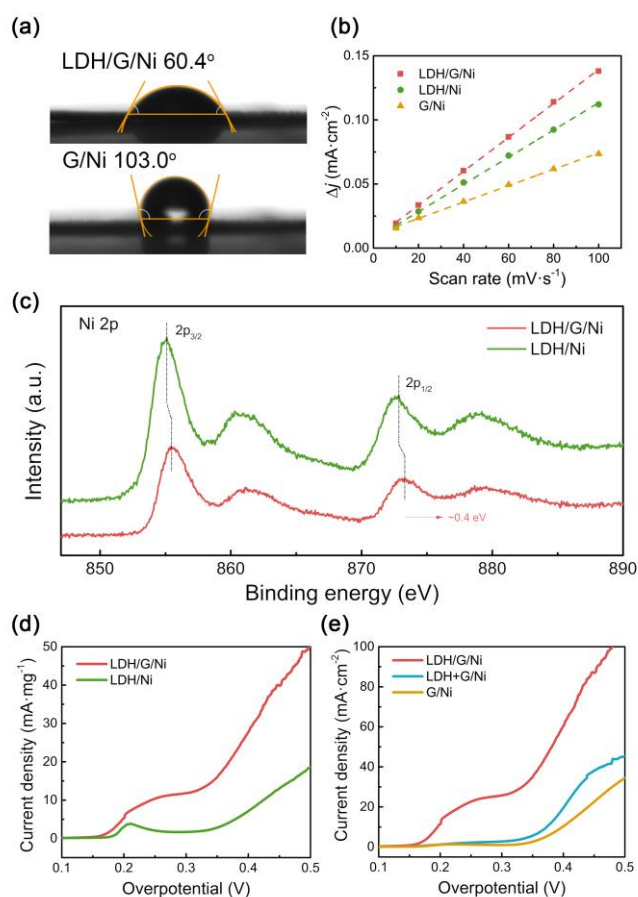


Fig. 3. The characterization of LDH/G/Ni electrocatalysts. (a) Contact angle tests of LDH/G/Ni and G/Ni electrocatalysts. (b) Charging current density differences plotted against scan rates. The linear slope, equivalent to twice of the double-layer capacitance C_{dl} , was employed to represent the ECSA. (c) High resolution Ni 2p spectra of LDH/G/Ni and LDH/Ni. (d) LSV plots of LDH/G/Ni and LDH/Ni. The specific current was calculated based on the loading amount of LDHs. (e) LSV plots of LDH/G/Ni, LDH+G/Ni and G/Ni. The scan rate for LSV plots was 10 mV s⁻¹. All the electrocatalytic tests were performed in O₂ saturated 0.1 M KOH solution.

On the other hand, the graphene layer, as an assistance of the 3D porous conductive network constructed by LDHs and Ni substrate, facilitated the Ni²⁺/Ni³⁺ redox during the linear sweep process (Fig. 2a). The high resolution Ni 2p spectra of LDH/G/Ni exhibited a ca. 0.4 eV shift to higher binding energy compared with LDH/Ni (Fig. 3c), which indicated that the graphene interface modulated the local electronic structure of Ni cations, and thus significantly promoted the OER activity of LDH/Ni. In addition, the graphene layer modulated the growth of LDHs and promoted its dispersion with a higher ECSA. A more-uniform and less-dense decoration of LDH sheets on substrate is expected to fully expose the active sites and deliver a much higher utilization efficiency of active sites. Fig. 3d compared the specific current densities based on the loading amount of LDHs for LDH/G/Ni and LDH/Ni. The LDH loading amount was obtained by thermogravimetric analysis (TGA, Fig. S5). The greatly larger current density of LDH/G/Ni indicated an improved utilization efficiency of NiFe LDHs with the existence of graphene. In the case of LDH/Ni, the LDH sheets grown on the Ni substrate were so serried and packed that part of the active sites were unaccessible and unutilized, even with a much higher hydrophilicity (Fig. S6). Thus, graphene not only promoted the OER activity of NiFe LDHs, but also ensured a high utilization efficiency of active sites in LDH/G/Ni. Additionally, distinguished from the reported inorganic/nanocarbon hybrid electrocatalysts,^{5, 20} the characteristic Ni substrate of LDH/G/Ni serves as a stable scaffold and a macroporous current collector, thus enhances the OER performance.

Furthermore, the *in situ* growth of NiFe LDHs on graphene above Ni substrate delivered a strong interfacial connection. To confirm it, a physical mixture of NiFe LDHs and G/Ni with the same LDH loading amount as LDH/G/Ni was fabricated, named as LDH+G/Ni, and Nafion was utilized as the binder. It's mentioned above that after a strong ultrasonic treatment for 60 min, the LDH/G/Ni block exhibited no significant change. In contrast, for LDH+G/Ni, the LDH sheets were washed off after the same treatment. As the LSV plots shown in Fig. 3e, LDH/G/Ni dramatically surpassed LDH+G/Ni. Meanwhile, the strong interaction was also demonstrated to enhance the stability of the catalyst (Fig. S7), and after long period of OER catalysis, the morphology of LDH/G/Ni mostly remained unchanged (Fig. S8). During the 8000 s chronoamperometric test, LDH/G/Ni showed high stability rival to LDH/Ni, indicating that the interfacial connection of LDHs to Ni with an ultra-thin graphene barrier was as strong as the direct connection of LDHs and Ni. The strongly coupled interface between LDH and graphene firmly anchored the LDH sheets and also facilitated the electron transfer from active phase to graphene and Ni substrate, thus substantially improving the catalysis performances.

The LDH/G/Ni complex was demonstrated to exhibit a superior and greatly enhanced OER catalysis activity, which was contributed from the novel structural features, especially the graphene incorporation. Firstly, the hydrophobic graphene modulated the growth behaviors of LDH on substrate towards

a uniform decoration, fully accessibility and higher utilization efficiency of active sites. Secondly, the highly conductive graphene layer in-between LDH and Ni substrate tuned the surficial physical or chemical characters and active states of both components, thereby improving the activity. The use of graphene made from graphene oxide reduction²¹ or CVD growth^{22, 23} is also reported to tune the interaction between the metal support and active electrode ($\text{Ni}_3\text{S}_2/\text{Co}_3\text{S}_4$,²¹ nickel cobalt binary hydroxides,²² or NiO ²³) for supercapacitors. Herein, the ultrathin graphene ensured a strong connection between LDHs and Ni substrate, which served as rapid electron pathway for superior OER reactivity.

3. Conclusions

A graphene barrier mediated hydroxide catalyst was proposed and exploited as a greatly effective OER electrode. With a regulated LDH hybridization, fully-exposed active sites, and strongly coupled interface attributed from the incorporation of graphene, the well-designed 3D hierarchical electrode exhibited a superior OER performance with a small onset overpotential of 240 mV, a low overpotential of 325 mV for 10 mA cm^{-2} and a decreased Tafel slope of 44 mV dec^{-1} in 0.1 M KOH. This work is helpful for the exploration of more efficient OER catalysts, and is also expected to inspire more research on the employment of graphene to modulate the interfacial features of various composites towards satisfactory applications in heterogeneous catalysis, energy conversion and storage, sensors and so on.

4. Experimental section

Synthesis of OER catalysts

The Ni foam was cut into small pieces of 1×1 cm, and cleaned in an ultrasonic washer using ethanol and deionized water for 10 minutes, orderly. The growth of porous graphene was operated in a tube furnace by CVD method.²⁴ Several pieces of cleaned Ni foam were placed in a quartz boat and then placed in the center of a horizontal quartz tube. The tube was then inserted into a furnace at atmospheric pressure. Under the protection of Ar (flow rate: 200 mL min^{-1}), the reactor was heated to 1000°C , and then H_2 (100 mL min^{-1}) were introduced into the quartz tube for 5 minutes to reduce the oxide layer. After the hydrogen treatment, 20 mL min^{-1} CH_4 was fed into the reactor for 5 minutes. Then the reactor was rapidly cooled to room temperature in the protection of Ar flow. The G/Ni foam was finally collected for further use.

The as-prepared graphene/Ni foam was then put into a 50 mL Teflon autoclave. A solution of 0.45 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.15 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1.0 g CTAB, 6.5 g water and 25.0 g methanol was decanted into the autoclave. This hydrothermal synthesis reactor was heated at 180°C for 24.0 h to enable the growth of NiFe LDH. At 180°C , methanol and nitrate ions react as follows: $4\text{CH}_3\text{OH} + \text{NO}_3^- \rightarrow 4\text{HCHO} + \text{NH}_3 + \text{OH}^- + \text{H}_2\text{O}$.¹⁷ The hydroxyl ions were released slowly, favorable to the uniformly

growth of NiFe LDH. After the hydrothermal treatment, the LDH/G/Ni was ultrasonic cleaned with deionized water for 10 minutes, then dried at room temperature for the following experiments. The LDH precipitate in the reactor was washed by deionized water in a suction filter, and reserved after natural drying.

The LDH/Ni catalyst was synthesized using pure Ni foam by the same method. The loading amount of LDHs on LDH/G/Ni and LDH/Ni is 2.18 and 3.63 mg cm^{-2} , respectively.

The LDH+G/Ni catalyst was obtained by dropping LDH suspension onto G/Ni foam. The suspension was prepared by mixing 5.0 mg p-LDH with 0.95 mL ethanol and 0.05 mL Nafion solution, then 1.0 h of ultrasonic treatment was applied to make the suspension more homogeneous. The dropping amount was determined by the LDH quantity on LDH/G/Ni. After the Ni foam was dried, the LDH was adhered on its surface.

Structural characterization

The morphology of the electrocatalysts were characterized using a JSM 7401F scanning electron microscope (SEM) operated at 3.0 kV and a JEM 2010 high-resolution transmission electron microscope (TEM) operated at 120.0 kV. Energy dispersive spectroscopy (EDS) analysis was performed at the acceleration voltage of 120.0 kV using a JEM 2010 TEM equipped with an Oxford Instrument energy dispersive spectrometer. The loading amount of LDH on LDH/G/Ni and LDH/Ni was obtained through thermogravimetric analysis (TGA) by a TGA/DSC1 STARe system under N_2 flow. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer at 40.0 kV and 120 mA with $\text{Cu-K}\alpha$ radiation. The contact angle was measured on OCAH200 Optical contact angle measuring instrument (Dataphysics, Germany).

Electrochemical performance evaluation

All electrochemical measurements were performed in a three-electrode system, using Pt sheet as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. Ni foam fastened to an electrode clip was used as the working electrode. This three-electrode system was controlled by a CHI 760D electrochemistry workstation (CH Instrument, USA) and the measurements were carried out in O_2 -saturated 0.1 M KOH solution. Before other measurements were applied, the catalyst was cycled several times by cyclic voltammetry (CV). The OER activities were tested by linear sweep voltammetry (LSV) at the scan rate of 10 mV s^{-1} . 95% iR-compensation was applied during the LSV and chronoamperometric test.

A constant potential was applied on the working electrode to decouple the catalyst oxidation and OER current. The catalyst oxidation current gradually dropped to zero in the first few seconds, and with the development of time, the current density will eventually approach a constant value, that is, the OER current density at the corresponding potential. By changing the given potential in a proper region, the correspondence between current density and potential was

obtained. For other samples, the same method was employed, and these voltammetry curves could be substitutes to the LSV plots adjacent to the onset potential.

Electrochemical active surface areas (ECSA) was determined by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammetry (CV). This measurement was performed on the same working electrodes among a potential window of 0.85–0.90 V vs. RHE and scan rates ranging from 10 to 100 mV s⁻¹. Then linear fitting of the charging current density differences ($\Delta j = j_a - j_c$ at the potential of 875 mV vs. RHE) against the scan rate was done. The slope is twice of the double-layer capacitance C_{dl} , which is used to represent ECSA.²⁵ The durability test was tested at η_{10} (the overpotential for 10 mA·cm⁻²) for each catalyst. The potential vs. RHE ($E_{vs. RHE}$) was calculated by the following equation: $E_{vs. RHE} = E_{vs. SCE} + 0.0592 \text{ pH} + 0.241$ ($E_{vs. SCE}$ stands for the potential vs. SCE) and the overpotential $\eta = E_{vs. RHE} - 1.229$.

Acknowledgements

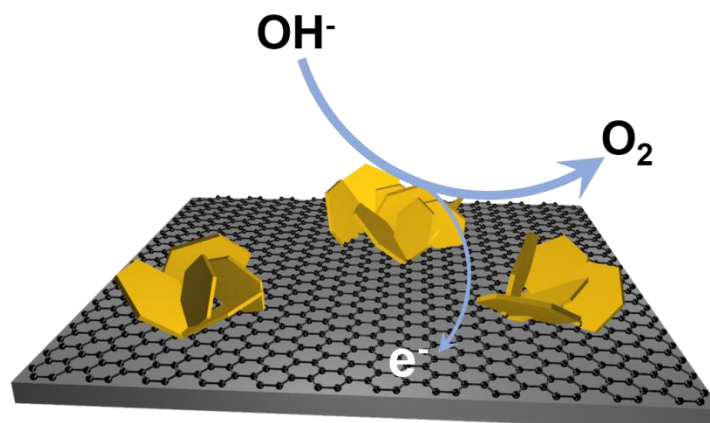
This work was supported by the Natural Scientific Foundation of China (No. 21306102 and 21422604) and Tsinghua University Initiative Scientific Research Program (2014z22076). We thanks helpful discussion from Jia-Le Shi and Han-Sen Wang.

Notes and references

1. Y. Jiao, Y. Zheng, M. Jaroniec and S. Z. Qiao, *Chem. Soc. Rev.*, 2015, **44**, 2060.
2. S. Trasatti, *Electrochim. Acta*, 1984, **29**, 1503; A. Rossi and J. F. C. Boodts, *J. Appl. Electrochem.*, 2002, **32**, 735.
3. D. Tang, J. Liu, X. Wu, R. Liu, X. Han, Y. Han, H. Huang, Y. Liu and Z. Kang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7918; M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei and H. Dai, *J. Am. Chem. Soc.*, 2013, **135**, 8452.
4. W. Ma, R. Ma, C. Wang, J. Liang, X. Liu, K. Zhou and T. Sasaki, *ACS Nano*, 2015, **9**, 1977; Z. Lu, W. Xu, W. Zhu, Q. Yang, X. Lei, J. Liu, Y. Li, X. Sun and X. Duan, *Chem. Commun.*, 2014, **50**, 6479; B. M. Hunter, J. D. Blakemore, M. Deimund, H. B. Gray, J. R. Winkler and A. M. Muller, *J. Am. Chem. Soc.*, 2014, **136**, 13118; L. Trotochaud, S. L. Young, J. K. Ranney and S. W. Boettcher, *J. Am. Chem. Soc.*, 2014, **136**, 6744; X. Lu and C. Zhao, *Nat. Commun.*, 2015, **6**, 6616; F. Song and X. Hu, *Nat. Commun.*, 2014, **5**, 4477; J. Nai, H. Yin, T. You, L. Zheng, J. Zhang, P. Wang, Z. Jin, Y. Tian, J. Liu, Z. Tang and L. Guo, *Adv. Energy Mater.*, 2015, **5**, 1401880.
5. X. Long, J. Li, S. Xiao, K. Yan, Z. Wang, H. Chen and S. Yang, *Angew. Chem. Int. Ed.*, 2014, **53**, 7584.
6. J. Jiang, A. Zhang, L. Li and L. Ai, *J. Power Sources*, 2015, **278**, 445.
7. X. Long, S. Xiao, Z. Wang, X. Zheng and S. Yang, *Chem. Commun.*, 2015, **51**, 1120; Y. Li, L. Zhang, X. Xiang, D. Yan and F. Li, *J. Mater. Chem. A*, 2014, **2**, 13250; F. Song and X. Hu, *J. Am. Chem. Soc.*, 2014, **136**, 16481; X. Zou, A. Goswami and T. Asefa, *J. Am. Chem. Soc.*, 2013, **135**, 17242.
8. Y. Li, K. Guo, J. Li, X. Dong, T. Yuan, X. Li and H. Yang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 20949; J. Landon, E. Demeter, N. İnoğlu, C. Keturakis, I. E. Wachs, R. Vasić, A. I. Frenkel and J. R. Kitchin, *ACS Catal.*, 2012, **2**, 1793; Y.-F. Li and A. Selloni, *ACS Catal.*, 2014, **4**, 1148; L. Kuai, J. Geng, C. Chen, E. Kan, Y. Liu, Q. Wang and B. Geng, *Angew. Chem. Int. Ed.*, 2014, **53**, 7547; T. Naresh Kumar, S. Sivabalan, N. Chandrasekaran and K. L. Phani, *Chem. Commun.*, 2015, **51**, 1922; A. M. Smith, L. Trotochaud, M. S. Burke and S. W. Boettcher, *Chem. Commun.*, 2015, **51**, 5261; J. Y. C. Chen, J. T. Miller, J. B. Gerken and S. S. Stahl, *Energy Environ. Sci.*, 2014, **7**, 1382; M. W. Louie and A. T. Bell, *J. Am. Chem. Soc.*, 2013, **135**, 12329; L. Wang, C. Lin, D. Huang, F. Zhang, M. Wang and J. Jin, *ACS Appl. Mater. Interfaces*, 2014, **6**, 10172; X. Zhong, H. Yu, G. Zhuang, Q. Li, X. Wang, Y. Zhu, L. Liu, X. Li, M. Dong and J.-g. Wang, *J. Mater. Chem. A*, 2014, **2**, 897; S. Chen and S.-Z. Qiao, *ACS Nano*, 2013, **7**, 10190; J. Wang, T. Qiu, X. Chen, Y. Lu and W. Yang, *J. Power Sources*, 2014, **268**, 341; Y. Hou, Z. Wen, S. Cui, S. Ci, S. Mao and J. Chen, *Adv. Funct. Mater.*, 2015, **25**, 872; S. Chen, J. Duan, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.*, 2013, **52**, 13567; J. Wang, H. X. Zhong, Y. L. Qin and X. B. Zhang, *Angew. Chem. Int. Ed.*, 2013, **52**, 5248; Y. Zhu, W. Zhou, Z. G. Chen, Y. Chen, C. Su, M. O. Tade and Z. Shao, *Angew. Chem. Int. Ed.*, 2015, **54**, 3897; S. Chen, J. Duan, W. Han and S. Z. Qiao, *Chem. Commun.*, 2014, **50**, 207; J. R. Galán-Mascarós, *ChemElectroChem*, 2015, **2**, 37; S. Chen, J. Duan, J. Ran, M. Jaroniec and S. Z. Qiao, *Energy Environ. Sci.*, 2013, **6**, 3693; S. Mao, Z. Wen, T. Huang, Y. Hou and J. Chen, *Energy Environ. Sci.*, 2014, **7**, 609; M. S. Burke, M. G. Kast, L. Trotochaud, A. M. Smith and S. W. Boettcher, *J. Am. Chem. Soc.*, 2015, **137**, 3638; W. Yuan, P. K. Shen and S. P. Jiang, *J. Mater. Chem. A*, 2014, **2**, 123; C. Jin, F. Lu, X. Cao, Z. Yang and R. Yang, *J. Mater. Chem. A*, 2013, **1**, 12170; X. Zhou, Z. Xia, Z. Zhang, Y. Ma and Y. Qu, *J. Mater. Chem. A*, 2014, **2**, 11799; T. Y. Ma, S. Dai, M. Jaroniec and S. Z. Qiao, *J. Am. Chem. Soc.*, 2014, **136**, 13925; M. Zhang, M. de Respinis and H. Frei, *Nat. Chem.*, 2014, **6**, 362; Z. Lu, H. Wang, D. Kong, K. Yan, P. C. Hsu, G. Zheng, H. Yao, Z. Liang, X. Sun and Y. Cui, *Nat. Commun.*, 2014, **5**, 4345; G.-L. Tian, Q. Zhang, B. Zhang, Y.-G. Jin, J.-Q. Huang, D. S. Su and F. Wei, *Adv. Funct. Mater.*, 2014, **24**, 5956; G.-L. Tian, M.-Q. Zhao, D. Yu, X.-Y. Kong, J.-Q. Huang, Q. Zhang and F. Wei, *Small*, 2014, **10**, 2251.
9. D. Friebe, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M. J. Cheng, D. Sokaras, T. C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Nørskov, A. Nilsson and A. T. Bell, *J. Am. Chem. Soc.*, 2015, **137**, 1305.
10. M. Gong and H. Dai, *Nano Res.*, 2014, **8**, 23.
11. Z. Zhao, H. Wu, H. He, X. Xu and Y. Jin, *Adv. Funct. Mater.*, 2014, **24**, 4698.
12. Y. Zhao, S. Chen, B. Sun, D. Su, X. Huang, H. Liu, Y. Yan, K. Sun and G. Wang, *Sci. Rep.*, 2015, **5**, 7629.
13. I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov and J. Rossmeisl, *ChemCatChem*, 2011, **3**, 1159.
14. Z. Wen, S. Ci, Y. Hou and J. Chen, *Angew. Chem. Int. Ed.*, 2014, **53**, 6496; W. Bian, Z. Yang, P. Strasser and R. Yang, *J. Power Sources*, 2014, **250**, 196.
15. W. Zhou, X.-J. Wu, X. Cao, X. Huang, C. Tan, J. Tian, H. Liu, J. Wang and H. Zhang, *Energy Environ. Sci.*, 2013, **6**, 2921.
16. Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei and H. M. Cheng, *Nat. Mater.*, 2011, **10**, 424.
17. H. Chen, L. Hu, M. Chen, Y. Yan and L. Wu, *Adv. Funct. Mater.*, 2014, **24**, 934.

18. M. Gao, W. Sheng, Z. Zhuang, Q. Fang, S. Gu, J. Jiang and Y. Yan, *J. Am. Chem. Soc.*, 2014, **136**, 7077.
19. C. C. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2013, **135**, 16977.
20. Y. Liang, Y. Li, H. Wang and H. Dai, *J. Am. Chem. Soc.*, 2013, **135**, 2013.
21. D. Ghosh and C. K. Das, *ACS Appl. Mater. Interfaces*, 2015, **7**, 1122.
22. Y. Bai, W. Wang, R. Wang, J. Sun and L. Gao, *J. Mater. Chem. A*, 2015, **3**, 12530-12538.
23. A. Bello, K. Makgopa, M. Fabiane, D. Dadoo-Ahrin, K. I. Ozoemena and N. Manyala, *J. Mater. Sci.*, 2013, **48**, 6707.
24. Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei and H. M. Cheng, *Nat. Mater.*, 2011, **10**, 424.
25. C. C. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2013, **135**, 16977.

Table of content



With a regulated hydroxide hybridization of the graphene barrier, the metal/graphene/hydroxide electrocatalyst exhibited superior reactivity for oxygen evolution.