Advanced Layered Double Hydroxide-Based Electrocatalysts for Electrocatalytic Oxygen Evolution Reaction

Tariq Ali,^a Niaz Muhammad,^b Tingzhou Yang,^a and Chenglin Yan^{*,a}

^a College of Energy, Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province, Key Laboratory of Advanced Optical Manufacturing Technologies of Jiangsu Province & Key Laboratory of Modern Optical Technologies of Education Ministry of China, Soochow University, Suzhou, Jiangsu 215006, China

^b Department of Chemistry, Abdul Wali Khan University, Mardan, Pakistan

Email: c.yan@suda.edu.cn (C. Y.)

Abstract Layered double hydroxides (LDHs) are the most promising candidates among all candidates for electrocatalytic water splitting, especially oxygen evolution reaction. Electrocatalytic activities of LDHs can be attuned by exfoliation, composition, morphology regulation and by intercalating some species. Moreover, exfoliation and flexible ion exchange can be tuned by the unique intercalation properties *via* flexible tunability of multiple metal cations. However, certain limitations like bulk thickness, large lateral size and low conductivity of LDHs decrease their uses in oxygen evolution reaction. In order to increase its electrocatalytic performances, researchers introduce different strategies such as combining the conductive materials to LDHs to introduce defects and tune the electronic structure of LDHs to enhance the active sites and increase intrinsic activity. In this minireview, we summarized current progress, strategies, challenges and prospective in the fabrication and designing of LDHs materials by various species.

Keywords layered double hydroxide, oxygen evolution reaction, electrocatalysts, tuning electronic structure, active sites

Introduction

Layered double hydroxides (LDHs) are considered as a favorable catalyst for electrocatalytic energy conversion and water splitting due to their good activity, low cost, high abundance and easy to scale up. LDHs have the general formulae $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{q+}(A^{n-})_{q/n}\cdot y\text{H}_2\text{O}$, in which M^{2+} and M^{3+} are metal cations and A^{n-} is a charge balance anion.^[1,2] Sometimes, M^{2+} and M^{3+} can be replaced with M^+ and M^{4+} for mono and tetravalent cations, respectively.^[1] Transition metal ions can improve the charge transport of materials. In the process of charge transport, electrons jump along with the layer due to the internal redox reaction of M^{2+} and M^{3+} . Metal cations have water and anions in their interlayers. These metal cations are responsible for the conduction and diffusion of water in its layers and ensure their close contact with electrocatalyst.^[3] In addition, gas products formed during the reaction is conducted by the layer spacing. The formulae show the highly tunable and flexible pheromones, M^{2+} , M^{3+} , and A^{n-} can bring widely used variation characteristics. In the preparation of LDHs, many advanced technologies and methods, such as hydrothermal, electrodeposition, chemical bath method, microwave-assisted, and ion-exchange methods have been applied and fruitful results have been achieved.^[4] LDHs normally show lamellar structure through one-step precipitation, which is consistent with inherent LDHs. More expose active sites or edges can appear during treatment of LDHs like exfoliation and cutting leads to enhanced catalytic activity due to the reduction in the diffusion length of ions and electrons.^[5] Wet chemical process is used to layered-by-layered structure from single-layered nanostructure as single-layered nanostructure can be used as a building block for LDHs.^[6] Additionally, another strategy to

produce defects in LDHs is engineering nanopores, which lead to a large number of high electrochemical active sites and also play a beneficial role in oxygen evolution reaction (OER) activity. Highly ordered defects are needed to ensure high stability in LDHs in nano and in micropores.^[7] Etching metal-ions such as Al, Ga and Zn to highly adjustable composition of LDHs carrier were used to obtain a number of nanopores. When LDHs containing carbonate is calcined in H_2 atmosphere, the nanopores in the host layer disappear, and the rehydration of the calcined product in aqueous KOH solution regenerates porous LDHs (control number of nanopores). LDHs with low conductivity from $10^{-13} \text{ S}\cdot\text{cm}^{-1}$ to $10^{-17} \text{ S}\cdot\text{cm}^{-1}$ hinders the ability to drive electrocatalytic OER activity, but it's a prerequisite for better conductivity for achieving significant OER performance.^[4] Hence, people try to overcome this limitation and find that it is a very effective way to improve the OER performance making the aggregates of LDHs with other conductive materials like carbon,^[8] metal sulfide,^[9] carbide,^[10] and nitride.^[11] Herein, we shortly discussed different synthetic techniques, replacement of anions by different functional groups to expand the interlayered distance to accelerate ions and exposed more active sites. Additionally, we also put a sight on layered by layered structure by exfoliating LDHs and assembling with layered materials. Herein, we also studied the host matrix of LDHs can also be tuned by the addition of metal ions like Mn, V, Cr, Mo, etc. While a nonconductive substance is combined with a conductive substrate like Ni foam, we also put an insight into the OER activity. Meanwhile, the synergistic effect due to the construction of a 3D hierarchical structure with the conductive backbone provides more active sites that have also been studied.

LDHs for OER

LDHs can be considered as metal-doped monometallic hydroxides because their structures are based on monometallic hydroxides. Although there are differences in types of interlayer ions (anions) participated, some basic principles of mono-metal hydroxides before introducing the LDH-OER catalyst will be presented. Conventional methods such as solvothermal and chemical deposition for synthesis of metal hydroxide catalysts usually nickel and cobalt hydroxide in the inert atmosphere were not carried out and the atmosphere of the reaction was exposed to air. During the process of crystal growth, the oxidation process induced by the dissolved oxygen in solution takes place and Ni^{2+} or Co^{2+} could be oxidized to be the trivalent counterparts without further oxidation treatment. These mono-metals hydroxides are positively charged and usually unbalanced. The synthesis of hydroxides in the air is basically "self-doped single metal LDHs", while the metal oxides prepared in inert condition is not oxidized, so their corridors have no interlayered anion and are charged balanced. Bulk Ni hydroxide with an hydrotalcite-like phase (α -phase) with an interlayer distance of 8.0 Å is active and has a divergent OER activity than the stable brucite-like phase (β -phase) with an interlayer distance of 4.6 Å.^[12,13] This phenomenon is caused by the difference of ion/ electron transfer characteristics due to the change of interlayer distance. In alkaline solution, a spontaneous transformation from $\alpha\text{-Ni}(\text{OH})_2$ to $\beta\text{-Ni}(\text{OH})_2$ occurs and experienced chemical aging process during charge/discharge. Many researchers have been devoted to OER of mono-metallic hydroxides of cobalt and nickel nature materials, but its electrocatalytic results are in arrears with the expectations. Gao *et al.* reported a superior OER catalysis of hollow nanosphered $\alpha\text{-Ni}(\text{OH})_2$ over the advanced RuO_2 catalysts.^[14] Controlled hydrothermal time reduced the thickness of $\text{Co}(\text{OH})_2$ nanocomposite, more active sites were exposed, and OER performance was improved reported by Tong *et al.*^[15] The influence of the structure of $\alpha\text{-Ni}(\text{OH})_2$ on OER performance was studied by Luan *et al.*^[16] The combination of metal elements with different valence states, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$, Ce^{3+} , Mo^{6+} , Mn^{2+} , V^{3+} , Cr^{3+} , into monometallic hydroxides is believed to be a general strategy to increase electrocatalytic intrinsic activity. O^{2-} (π -donor) π -symmetric localized electrons can be redistributed by bridging to endow oxide species with good absorption/desorption ability.^[17] However, the real function of the metallic center, the verification of chemical state and the kind of surface effect for a cause in OER process are still under debate. In addition, it is a reasonable and replaceable strategy to change the electronic structure of hydroxides by substituting non-metals (such as sulfur, phosphorus, fluorine and boron) for lattice oxygen in metal hydroxides. However, the control of the synthesis process is quite difficult. Different types of LDHs materials for OER are shown in Scheme 1.

LDHs Based on Number of Metal Elements

Bimetallic LDHs

Transition metals can also increase the catalytic activity of OER by increasing the active sites and by adjusting the electronic structure of LDHs. Chen *et al.* regulate the electronic structure of $\text{Co}(\text{OH})_2$ by doping heteroatom (Cu, Mn), and then the positive charge of matrix metal ion ($\text{Co}^{(2+\delta)+}$, $0 < \delta < 1$) is enhanced, which improves the OER performance.^[18] After Cu doping, the valence state of $\text{Co}^{(2+\delta)+}$ formed in $\text{CuCo}(\text{OH})_2$ is higher than that of pristine or Mn-doped $\text{Co}(\text{OH})_2$, which greatly reduces the energy barrier formed in OER during Co-OOH steps by $\text{Co}^{(2+\delta)+}\text{-OH}_{\text{ad}}$. In addition, it is reported that the hollow

Scheme 1 Different types of LDHs for OER

structure of LDHs has an efficient effect on OER. Zhang and coworkers reported a hollow structured microsphere NiFe LDH (NiFe HMS) with 250 nm of diameter, which composed of ultra-thin NiFe LDH nanoplates (NiFe LDH NP).^[19] The ultra-thin hollow structure NiFe LDH has some advantages including high specific surface area, good ion/electron transport hydrophilicity, and better performance than the conventional NiFe LDH. Todoroki *et al.* synthesized heterogeneous layered nanostructures with high activity of NiFe hydroxide/oxide on 316 stainless steel (SS) substrate under constant current density electrolysis for OER.^[20] The hetero film composed of NiFe hydroxide nanofibers on the NiFe oxide buffer layer shows OER potential at 20 °C at 10 $\text{mA}\cdot\text{cm}^{-2}$ of 254 mV, and OER performance is better than that of NiFe LDH catalyst in the high current density region greater than 100 $\text{mA}\cdot\text{cm}^{-2}$. Peng and co-workers theoretically studied the OER process of NiFe LDH.^[21] They find a higher OER activity for Fe edge sites than Ni. They proposed that the controlled growth of Fe edge sites can be induced by acid etching method for higher OER activity. Dong *et al.* intercalated NiFe LDHs with dicarboxylates anions and found the substrate anion intercalation has higher OER activity.^[22] Ye *et al.* assembled NiFe LDH hollow nano prism by ultra-thin NiFe LDH nanosheet using a simple self-template strategy.^[23] Additionally, Zn introduction to ZnCo LDH is also considered as another strategy to electrocatalytic OER activity.^[24] Due to the inertness of Zn to OER, Zn alone cannot play a catalytic role, but the alternating arrangements of Zn and Co could improve the interactions between reactants and active sites, further stimulating the catalytic reaction. In addition, defect engineering is also an effective strategy on an atomic scale. By etching amphoteric metallic elements like Al, Ga and Zn, into LDH host, different unsaturated coordination metal sites are created, so as to improve the catalytic activity by the reduction of Gibbs free energy in OER process. Zhou *et al.* reported defects rich Fe doped Ni and Co hydroxides by general cation exchange.^[25] Due to the oxidation of Ni^{2+} or Co^{2+} by Fe^{3+} , it can be etched in the main layer of corresponding LDHs, resulting in various nanopores defects and grained boundaries including vacancies of Ni, Co and oxygen vacancies after the dissolution of $\text{Ni}^{2+}/\text{Co}^{2+}$ in the basal plane. Li *et al.* introduced O-vacancies quantitatively in FeNi-LDH on Ni foam by intercalation of NaCl at ambient conditions.^[26] A higher range of oxygen vacancies (1.3%—27.4%) can be produced by the removal of Na^+ cation from FeNi LDH. O-vacancy has good conductivity, the surface wettability of electrolyte and

adsorption and activation ability of FeNiLDH/NF. Zhao *et al.* used a one-step precipitation process of Co^{2+} and Fe^{3+} for the preparation of CoFe LDHs.^[27] The optimized structure endows them for higher activity of OER in 1 M KOH. Higher activity of overpotential of 262 mV at a current density of $10 \text{ mV}\cdot\text{cm}^{-2}$ of Co_8Fe_1 LDH is dedicated to the optimal composition and synergic effect. Cui *et al.* fabricated an efficient LDH based OER catalyst by a self-template method.^[28] Due to the defect enhanced structure and excellent charge transport capability, the defect CoFe LDHs has significant OER activity and good stability. According to EIS data, the time constant of OER at microporous defects is several orders of magnitude smaller than that of CoFe LDHs surface, which certify that electrocatalytic activity derived from the micropore defect. Fan *et al.* formed NiV LDH ultrathin nanosheets with a thickness of less than 1 nm by host containing vanadium $\text{Ni}(\text{OH})_2$.^[29] The free energy landscape of adsorption of intermediate products H_2O , $^*\text{OH}$, $^*\text{O}$ and $^*\text{OOH}$ on $\text{Ni}_{0.75}\text{V}_{0.25}\text{LDH}$ and $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{LDH}$ confirmed the reduction of barrier in the speed limit step (from $^*\text{OH}$ to $^*\text{O}$ or from $^*\text{O}$ to $^*\text{OOH}$). The free energy landscape of the reaction intermediates is shown in Figure 1. Oxygen is singly bonded to the intermediate species $^*\text{OH}$ and $^*\text{OOH}$ on the surface. The constant for binding energy is 3.22 eV. The rate-limiting step in calculated free energy landscape is the formation of $^*\text{OOH}$, while the sample is doped with V at a potential $\eta = 0.62 \text{ V}$. The formation of $^*\text{O}$ is the rate-limiting step when sample is doped with Fe at $\eta = 1.28 \text{ V}$. The OER performance can be significantly improved by Fe incorporation to $\text{Ni}(\text{OH})_2$, i.e., the formation of NiFe LDH. As an operative OER catalyst, NiFe based LDH has been widely studied, but the mechanism of Fe doping and its effect on OER activity are still controversial.

Figure 1 DFT calculation. Adsorption geometries of the intermediates H_2O , $^*\text{OH}$, $^*\text{O}$ and $^*\text{OOH}$ in (a), (b), (c) and (d), respectively. The red, blue, white, grey atoms represent the O, Ni, H and V atoms, respectively. The adsorption structures are similar to these when one Ni is substituted by Fe instead of V; (e) the free-energy landscape.^[29] Copyright © 2016, Springer Nature

Trimetallic LDHs

Due to the highly flexible composition of LDHs, it is easy to introduce the number of active centers to the structure to modify the active species and electronic structure of LDH. Therefore, many LDHs, especially NiFe LDH, showed activity to OER. However, it's not very close to the demanding optimal state. To overcome this challenge and promote the electrocatalytic activity of OER, a third type of metal doping is introduced. It can be further improved by doping a third metal. The addition of dopants can adjust the electronic structure of the original LDH, enhance the cooperation between the dopant metal and the host metal, and form the trimetallic LDH with high electrocatalytic activity. Recently, Li *et al.* used one step hydrothermal method to prepare the ultra-thin NiFeV array.^[30] The electronic structure of NiFe LDH was modulated by adding V (V^{3+} , V^{4+} , V^{5+}) into the layered structure, which improved the

conductivity of NiFe LDH. Cr doping in LDHs can produce stronger electronic interactions within the metal hydroxide matrix due to multiple oxidation states (from +1 to +6), which enhances the synergy between metals leads to improve OER activity.^[31] In addition, Cr^{3+} and Cr^{4+} (or even 5) in the oxidized state can contribute to the sequence reaction of OER because of the action of active species like Ni and Fe. Xu and co-workers reported 3D porous $\text{Ni}_6\text{Fe}_2\text{W}_x\text{-LDH}$ electrocatalyst by a one-step synthesis for OER.^[32] $\text{Ni}_6\text{Fe}_2\text{W}_x\text{-LDH}$ has abundant defects edge active sites with porosity. The introduced tungsten is proved to be in W^{6+} oxidation state, which can promote charge transfer and electron capture, thus reducing the critical transition barrier of OH to O radicals adsorbed in OER. In addition, the 3D nanostructures of $\text{Ni}_6\text{Fe}_2\text{O}_2\text{OH}$ grown vertically on the surface of the nanosheet and self-supported on the carbon fiber substrate contribute to the penetration of the electrolyte and the enhancement of the conductivity. Based on the optimization of structure and composition, the prepared $\text{Ni}_6\text{Fe}_2\text{W-LDH@CC}$ (carbon fiber cloth) electrode showed excellent OER activity at a low overpotential of 264 mV and a Tafel slope of $44.5 \text{ mV}\cdot\text{dec}^{-1}$ at $10 \text{ mA}\cdot\text{cm}^{-2}$. Xu *et al.* prepared Ce doped NiFe LDHs with significant OER activity by rich redox performance flexible coordination number (Ce^{3+}).^[33] Song *et al.* introduced sintering and ball by ball milling method for preparing high-efficiency oxygen evolution catalyst.^[34] Highly porous $\text{Ni}_{1-x}\text{Fe}_x\text{Se}_{1.15}$ bulk electrode was obtained by grinding aid of Se via sintering. Active $\text{Ni}_{1-x}\text{Fe}_x$ LDH was prepared by electrochemical oxidation on $\text{Ni}_{1-x}\text{Fe}_x\text{Se}_{1.15}$ surface. This process has the advantages of substrate-free, high mechanical strength and low cost. In addition, Mn and V doping in $\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-LDH}$ shows an excellent OER performance with current density reached 1000 and $100 \text{ mA}\cdot\text{cm}^{-2}$ and an overpotential of 300 and 244 mV in 1 M KOH, respectively. V-doping promotes the OER kinetics by promoting the electron transfer at electrode/electrolyte interface.

LDHs Based on Structure

3D carbon-based hierarchical LDH based materials

As a typical 2D material, graphene with excellent electrical conductivity is used as a coupling substance of LDHs producing electrocatalysts with significant catalytic properties for OER. Coupled graphene not only endows LDH composite with special physical and chemical possessions, but also involves in electrocatalytic performance.^[35] Qiao group prepared 3D hydrophilic N doped graphene hydrogel catalysts (NG-NiCo) by doping N on NiCo LDH.^[36] Due to a large number of functional groups, NG-NiCo shows remarkable OER activity. These functional groups provide a 3D porous framework, reduce catalyst's internal resistance, promote the adsorption capability of reaction intermediates and exposing many active sites, which is conducive to the release of oxygen. Chen *et al.* prepared an ultrafine fiber electrode composed of CNTs and NiFe LDH nanoparticles and achieved a stable and significant OER activity under the action of catalyst.^[37] Under higher current density, this type of microfiber electrode increases the surface area, enhances the substrate-electrocatalysts contact, and the use of binders like polytetrafluoroethylene and Nafion. For the first time, nanocarbon and ultrafine amorphous NiFe LDH ($< 5 \text{ nm}$) was synthesized using carbon and metal source molecular precursors using one-pot method by Yin *et al.*^[38] In this case, excellent intrinsic OER activity was achieved by confinement of nanohybrid to a single sheet. The enhancement in OER activity is attributed to the increase in the active surface area, twisted structure and strong coupling of N doped carbon with active phase of LDH.

3D hierarchical nanostructures of LDHs/metal

In order to develop LDHs into an efficient OER electrocatalyst, hollow structure engineering, nanosheet array preparation, porous structure design, and other technologies have been developed.^[39] Due to the limitations of LDH nanostructures and poor conductivity, no matter what effective preparation technology is used, there is no remarkable success in the achievement of significant OER activity. In order to overcome this challenge, a highly conductive framework was proposed to grow LDH nanostructures as a current collector. Zhang *et al.* achieved a higher OER activity (6 times) higher than NiFe LDH by decorating Au single atom by 0.4 wt%.^[40] Au atom redistributes the charge on active Fe and the atoms in its surroundings on NiFe LDH. Zhu *et al.* significantly improved the OER activity by incorporation of Au nanoparticles on NiFe LDH nanosheets.^[41] Highly electronegative Au accelerates the synthesis of intermediate species (*i.e.*, OOH) by transforming the stable and generated Ni cation to higher oxidation state (Ni³⁺) and also increase the electron transfer rate. Additionally, coaxial nanotube arrays were formed by the electrodeposition of NiCo LDH nanosheets.^[42] The enhanced OER performance was assigned to the synergism among active LDH and Ni metal, fast charge transfer to transition metal in LDH from electronegative metal produce metal cation with higher oxidation state and electron transferred by highly conductive metal.

Metal organic framework based LDHs

Due to its adjustable structure and function, metal-organic framework (MOFs) has been widely used in sensing, molecular separation and energy storage, with large surface area and highly ordered pores, which has become a useful precursor for the preparation of high-performance energy storage materials. Because of the ordered porosity and adjustable structure of the MOF precursor, it is easy to prepare a porous, hollow and even more complex structure of electroactive materials by using MOF precursor. Hollow MOF derivatives are considered to be ideal materials for obtaining high capacity due to their abundant reaction sites. For example, Wang *et al.* prepared NiCo LDH hollow microspheres by controlled chemical etching/growth method of zeolitic imidazolate framework-67 (ZIF-67), which served as a sacrificial template and a precursor.^[43] Chen *et al.* prepared ultrathin NiFe-MOFs nanosheets on 3D conductive nickel foam.^[44] They introduce a strategy of *in situ* growth of ultrathin nanosheet arrays of 2D MOF on various supports as shown in Figure 2. The prepared materials showed attractive catalytic properties, challenging the concept that MOFs itself is an inert catalyst for electrochemical reaction. For heterogeneous electrocatalytic processes such as OER, the activity of electrocatalyst depends not only on its intrinsic composition and conductivity, but also on the electrode geometry, structural porosity, accessible active center and interface coupling of the used catalyst. It has become a hot spot in the research of electrochemical reactions that active components are directly added to the 3D porous conductive scaffolds to directly construct the graded electrocatalysts. Compared with the 2D planar or granular electrocatalyst prepared on the glassy carbon electrode, the electrode with 3D porous conductive structure possesses the advantages of good conductivity to electron transport and large electrochemical active surface and fully exposed active site, which is conducive to electrolyte penetration and bubble separation. Xu *et al.* propose a strategy to design a novel 3D hierarchical ZIF-67/CoNiAlLDH/NF electrocatalyst by the combination of unique properties of LDHs and MOFs materials.^[45] CoNiAl LDH nanoplates were grown on conductive surface of 3D Ni foam

through hydrothermal method followed by the deposition of ZIF-67 nanocrystals on LDH nanoplates surface. A crystalline-dissolution-recrystallization method was used to integrate 2D ZIF-67. ZIF-67/CoNiAl LDH/NF is a good candidate for OER due to exposed active sites, electrically conductive porous skeleton and strong coupled interfaces. Zhang *et al.* prepared a series of oxalate MOFs grown on Cu foils and converted them to LDHs via alkaline treatments trimetallic FeCo_{0.5}Ni_{0.5} LDH, which shows an OER activity with an overpotential of 248 mV AT 10 mA·cm⁻² current density.^[46] FeCo_{0.5}Ni_{0.5} LDH shows a Tafel slope of 38 mV·dec⁻¹. Le *et al.* boost up electrocatalytic kinetics of hollow (Co, Ni)Se₂ nanocages by treating ZIF-67 by ion-exchange method and synthesized followed by decoration with NiFe LDHs.^[47] Fe and Ni can optimize the π -symmetric electron partial delocalization at the interface and adsorption/desorption property of oxygen species, which take part in enhanced OER. By using the homogeneous distribution of hollow NiCo LDHs (H-LDHS) derived from ZIF-67 on a hollow carbon spherical shell, the hollow type (HIH-LDH) was successfully prepared by Lee *et al.*^[48]

Figure 2 (a) Synthetic process of metal-organic framework nanosheet array. Metal salts and substrate are firstly mixed together in an aqueous solution, and then introduces the organic ligand. Next, the MOF nanosheet array grows on the surface of substrate via a dissolution-crystallization mechanism.^[44] Copyright © 2017, Springer Nature.

HCS@ZIF-67 was prepared by growing ZIF-67s on HCS shell and transforming it into H-LDHs by Ni salt hydrothermal treatment. Chen *et al.* proposed a simple pseudoreplication method of 2D ZIF-67 nanosheet grafted with 3D ZIF-67 polyhedron on CC surface. Then the samples were pyrolyzed at low temperatures to obtain 2D N-doped carbon nanosheets and 3D N-doped hollow carbon polyhedron (Co@N-CS/N-HCP@CC) Co nanoparticles.^[49] Fast charge transfer, rich catalytic active centers of *in-situ* ultrathin 2D nanosheets of the catalyst are the advantages for higher water splitting capabilities. The coupling porous 3D hollow polyhedron has high structural stability with a high mass transfer capability. The supported CC not only greatly enhances the electrical conductivity and mechanical flexibility of the electrode, but also inhibits the possible aggregation or self-stacking of 2D and 3D subunits. The synergistic effect of C, N and Co makes the hydrogen adsorption on the active surface site to be the best. When the current density is 10 mA·cm⁻², the overpotential of the catalyst is 248 mV.

LDHs Based Electrocatalysts

Metal oxides, hydroxides, and oxyhydroxides

A 3D channel can be constructed by the given derivatives of LDH-based materials, which are sulfides, nitrides, oxides, selenides, borides, carbides, borates, and phosphides, having rapid electron transfer with a high electrochemically active surface area. Some materials like the oxides of ruthenium and

iridium have been found as a highly OER active electrocatalyst, but they have very limited resources like poor stability and high cost hinder their scale-up. While competitive electro-catalytic properties belong to transition metals of the first row, *e.g.*, oxides, hydroxides, and oxyhydroxides. Wu *et al.* prepared binder-free hierarchical Ni/NiO@CoFe LDH electrocatalyst for water splitting by a two-step strategy.^[50] Laser ablation on Ni foam was used for a few tens of seconds to prepare Ni/NiO micro/nanostructure followed by the deposition of CoFe LDH by electrodeposition. The Ni/NiO@CoFe LDH catalyst served as a binder-free nanostructured catalyst with efficient performance in OER. Xie *et al.* prepared well-distributed nanopores by Ostwald ripening process.^[51] Ultrathin nanomesh structure of β -(Ni(OH)₂) facilitates ion penetration, the charge transport, gas release similarly good practice in OER process for volume changes in buffer. The enhanced OER activity of β -(Ni(OH)₂) is based on ultrathin nanomesh disclosed structure, leads to easy contact with electrolyte, abundant and scattered accumulated nanopores in more active phase and more permeable channels due to multiple nanopores in nanomesh. Due to the single-crystalline nature of β -(Ni(OH)₂) nanomeshes, the charge transport in 2D basal plane is accelerated on the bases of expansion and faulty deformations in continues OER activity. Xu *et al.* coated a thin layer of Ni(oxy)hydroxide on a porous Fe(oxy)hydroxide on carbon paper (CP) and developed Fe-rich OER catalyst.^[52] Fe and Ni can interplay on a large area on the surface lead to charge transfer. Fe 2p XPS spectra of Fe/CP and Ni/Fe/CP two characteristic peaks of Fe²⁺ and Fe³⁺. Figure 3a shows Fe³⁺ peak for Fe/CP is positively shifted for Ni/Fe/CP by 0.5 eV. Ni 2p XPS spectra are shown in figure 3b. in this case, Ni²⁺ main peak for Ni/Fe/CP shows negative shift by 0.5 eV compared to Ni/CP. Therefore, the opposite binding energy transfer between Ni 2p and Fe 2p is due to the extraction of electrons from the Fe layer through the interface to the Ni layer. catalytic activity of Ni/Fe/CP, because the high valence state of

Figure 3 (a) Fe 2p XPS spectra of Fe/CP and Ni/Fe/CP. (b) Ni 2p XPS spectra of Ni/CP and Ni/Fe/CP.^[52] Copyright © 2019, American Chemical Society.

Ni has been confirmed as the active center of OER. The covalency of Ni—O bond increases with the increase of Ni valence. More covalency of Ni—O leads to more oxygen characteristics, which can be proved to improve OER activity. The prepared sample shows the best OER activity of overpotential of 223 mV at a current density of 10 mA·cm⁻² at the Tafel slope of 32.5 mV·dec⁻¹.

Transformation and etching methodologies were used to obtain Fe-CoOOH/G (graphene) nanoparticles.^[53] Metal ions such as Al³⁺, Co²⁺ and Fe²⁺ were used to promote electrostatic interactions. These ions were absorbed on the graphene oxide (GO) surface for the easy growth of CoFeAl-LDH on GO sheet (CoFeAl-LDH/G) under reflux condition. Afterward, Al³⁺ ion was removed after 12 h treatment in alkali solution and etched to CoFe-LDH/G forming having hierarchical porous structure leading to the formation of oxyhydroxide from hydroxides (Fe-CoOOH/G, the average pore size of 9.9 nm and specific surface area of 238 m²·g⁻¹). Fe-CoOOH/G shows an excellent OER activity of 330 mV at 10 mA·cm⁻² in 1 M KOH. Aforesaid data confirmed the improved catalytic OER activity due to morphological changes in the structure of LDHs, its components, electronic structure on the surface and its surface reactivity of metallic oxides.

Bimetallic nitrides and phosphides

In the past few years, transition metal phosphides (TMP) materials are believed to be an excellent and competitive OER catalysts for high efficiency and low cost. TMPs would drive LDHs structurally and compositionally and functionally by the addition of another element for better OER activities.^[54] Zhang *et al.* prepared *in-situ* TMPs nanosheets based on CoFe LDHs precursor by treating with phosphating agent (NaH₂PO₂).^[55] Phosphidation leads to tailoring the thickness and crystallinity improvements. The advantages of ultrathin amorphous CoFeP nanosheets are more exposed active sites due to lower thickness, regulated and tuned electronic structure due to metal-P chemical bond and oxygen defects sites and controlled thickness due to different degree of partial phosphating. Hu and coworkers synthesized bimetallic (Fe_xNi_{1-x})₂P nanoarrays for OER activity in an alkaline solution.^[56] Based on to embed extra metal, lead OER activity at an overpotential of 156 mV at current density 10 mA·cm⁻² and 255 mV at a current density of 500 mA·cm⁻² in 1 M KOH. Wu and co-workers introduced transition metals nitrides (Ni₃N) nanosheets for highly OER electrocatalytic activity.^[57] Bimetallic TMNs broadly increases the activity of OER and HER, hence, LDHs play an important role in bimetallic TMNs for water splitting applications. An overpotential of 280 mV is achieved at a current density of 10 mA·cm⁻² for bimetallic Ni₃FeN-NPs.^[58] A negative effect is shown, while bimetallic nitrides are placed on 3D support for improving the catalytic activity. NiFe bimetal nitrides grown on a substrate like Ni foam can solve the problem.^[59] FeNi₃N/NF electrocatalysts show an enormous OER activity of 202 mV at a current density of 10 mA·cm⁻² with a Tafel slope of 40 mV·dec⁻¹.

Bimetal sulfides/selenides

Widely research has been done on transition metal dichalcogenides (TMDs) especially MoS₂ in order to dope other metal atom and activate the basal plane.^[60] Fe doping can tune the OER performance by tuning the electronic structure of Ni-O/OH. OER activity of some electrocatalysts can be enhanced and tuned by the sulfide's addition to bifunctional catalysts.^[61] Since bimetallic catalysts show excellent performance than monometallic catalysts, LDHs provide a better platform as an electrocatalyst for bimetallic catalysts. The excellent achievement in the field of catalysis is in the formation

of oxides and hydroxides on the TMDs surface during the oxidation.^[62] Xiong *et al.* studied three kinds of superlattices (MoS₂/NiFe LDH, MoS₂/G and NiFe LDH/G) for electrochemical water splitting and found significance OER and HER activity.^[63] They found that MoS₂/LDH superlattices had superior OER activity than the rest due to alternative restacked unilamellar metallic MoS₂ and LDH nanosheets. The active sites of TMDs can be notified by comparing the TEM images of TMDs in OER processes. Some results showed a thin hydroxide or oxide formation occurred on the top of TMDs and they are believed to be the real active sites taking part in OER performance. During OER conditions, metal selenides were unstable while nickel selenide can form nickel hydroxides. The oxides and hydroxides on the surface of TMDs are still believed to be the real active sites for electrocatalytic OER (Table 1).

Table 1 Electrochemical OER activities of some LDH based electrocatalyst

Catalyst	Overpotential [mV]@ 10 mA·cm ⁻²	Tafel Slope/ (mV·dec ⁻¹)	Medium	Ref.
Co(OH) ₂	327	78	1 M KOH	[15]
Ni(OH) ₂ -NP ^a	260	78.6	1 M KOH	[16]
Ni ₃ Fe _{1-x} V _x /CFP ^b	200	39	1 M KOH	[17]
Cu-Co(OH) ₂	300	47	1 M KOH	[18]
Ni-Fe LDH	254		1 M KOH	[20]
NiFe LDH-A50 ^c	308	50	1 M KOH	[21]
P-NFSHPs ^d	255	56	1 M KOH	[23]
Ni _{0.83} Fe _{0.17} (OH) ₂	245	61	1 M KOH	[25]
NiFeV LDHs	195 [*]	42	1 M KOH	[30]
Ni ₆ Fe ₂ W-LDH @CFP	264	44.5	1 M KOH	[32]
Ni _{0.67} Fe _{0.33} /C	210	35.1	1 M KOH	[38]
^s Au/NiFe LDH ^e	237	< 40	1 M KOH	[40]
NiFe-MOF	240	34	1 M KOH	[44]
FeCo _{0.5} Ni _{0.5} -LDH	248	38	1 M KOH	[46]
Ni/NiO@CoFe LDH	230	34.3	1 M KOH	[50]
(Fe _{0.5} Ni _{0.5}) ₂ P	156	66	1 M KOH	[56]
MoS ₂ /NiFe-LDH	210	77	1 M KOH	[63]

^a Pt-like Ni(OH)₂-NP. ^b Carbon fiber paper. ^c NiFe LDH treated with 50 μL of 1 M HNO₃. ^d Polyvinyl-pyrrolidone (PVP)-decorated nickel-iron diselenide hollow nanoparticles. ^e Single-atom Au supported on NiFe LDH. ^{*} Overpotential of 20 mA·cm⁻².

Conclusions and Perspectives

LDHs materials and their derivatives play a remarkable role in the catalytic activity of OER due to sustainable interlayered anion, high flexibility, tunable 2D lamellar structure, various components and diversity in intrinsic electronic structure. High efficiency metal based OER electrocatalyst can give maximum active site, ideal charge transfer or mass diffusion ability, and accelerate the adsorption of oxygen intermediates on the catalyst surface through nanostructure and surface engineering. In this minireview, we shortly discussed different synthetic techniques, replacement of anions by different functional groups to expand the interlayered distance to accelerate ions and exposed more active sites. Additionally, we also put a sight on layered by layered structure by exfoliating LDHs and

assembling with layered materials. Herein, we also studied the host matrix of LDHs can also be tuned by the addition of metal ions like Mn, V, Cr, Mo, etc. The introduction of Mo, Mn, Fe, Co and other heteroatoms to prepare alloy or composite materials has been established as an effective strategy to improve the intrinsic activity. In addition, we also put an insight into the OER activity while a nonconductive substance is combined with a conductive substrate like Ni foam. Meanwhile, the synergistic effect due to the construction of a 3D hierarchical structure with the conductive backbone provides more active sites that have also been studied. Non-metallic components such as carbon based materials (carbon nanotubes, reduced graphene and graphitic carbon nitride) and carbon based substrates (carbon fiber cloth or paper) can improve the charge transfer or mass diffusion ability of OER by hybridization.

Challenges such as unsatisfactory long-term durability and achieving long-current electrolysis need to be fixed in the coming years to achieve the requirements of practical applications in industrial scale. To construct a 3D hierarchical electrode, the fine integration of LDHs and 2D MOFs into a conductive scaffold remains also a big challenge in the process of OER. For the layered structure of LDHs, it is very critical and challenging to understand the relationship between metal components and active centers in the matrix layer and the influence of interlayer anions on catalytic activity. In the process of OER catalysis, it is helpful to study the changes of the composition and chemical state of metal ions in LDHs, to recognize the real active site or the transformation of the active site of metal ions in LDHs. However, it is still a great challenge to control the electronic structure of LDHs by manipulating the layered structure. It is feasible to better control the type and number of active centers and the corresponding catalytic kinetics. The industrial application of LDHs in OER process is hindered by different factors in synthesis process, reaction direction in OER process, unexpected reaction and long-term durability hazards.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 21603157), the College Natural Science Foundation of Jiangsu Province (Nos. 16KJB430025, BK20181168), and the Postdoctoral Science Foundation of China (Nos. 2016T90488, 2015M580459).

Conflict of Interest

The authors declare no conflict of interest.

Copyright © 2020 Tariq Ali, Niaz Muhammad, Tingzhou Yang, and Chenglin Yan. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). The use, distribution or reproduction in other forums is permitted, provided the original author(s) or licensor are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.

References

- [1] Fan, G.; Li, F.; Evans, D. G.; Duan, X. *Chem. Soc. Rev.* **2014**, *43*, 7040.
- [2] Yu, L.; Zhou, H.; Sun, J.; Qin, F.; Luo, D.; Xie, L.; Yu, F.; Bao, J.; Li, Y.; Yu, Y. *Nano Energy* **2017**, *41*, 327.
- [3] Zhao, Y.; Jia, X.; Waterhouse, G. I.; Wu, L. Z.; Tung, C. H.; O'Hare, D.; Zhang, T. *Adv. Energy Mat.* **2016**, *6*, 1501974.
- [4] Hall, D. S.; Lockwood, D. J.; Bock, C.; MacDougall, B. R. *Proc. R.*

- Soc. Edinb. Sect. A-Math. **2015**, 471, 20140792.
- [5] Nicolosi, V.; Chhowalla, M.; Kanatzidis, M. G.; Strano, M. S.; Coleman, J. N. *Science* **2013**, 340, 1226419.
 - [6] Dong, X.; Wang, L.; Wang, D.; Li, C.; Jin, J. *Langmuir* **2011**, 28, 293.
 - [7] Li, Z.; Duan, H.; Shao, M.; Li, J.; O'Hare, D.; Wei, M.; Wang, Z. L. *Chem* **2018**, 4, 2168.
 - [8] Ping, J.; Wang, Y.; Lu, Q.; Chen, B.; Chen, J.; Huang, Y.; Ma, Q.; Tan, C.; Yang, J.; Cao, X. *Adv. Mater.* **2016**, 28, 7640.
 - [9] Liu, J.; Wang, J.; Zhang, B.; Ruan, Y.; Lv, L.; Ji, X.; Xu, K.; Miao, L.; Jiang, J. *ACS Appl. Mater. Interfaces* **2017**, 9, 15364.
 - [10] Hao, N.; Wei, Y.; Wang, J.; Wang, Z.; Zhu, Z.; Zhao, S.; Han, M.; Huang, X. *RSC Adv.* **2018**, 8, 20576.
 - [11] Wang, L.; Dionigi, F.; Nguyen, N. T.; Kirchgeorg, R.; Gliech, M.; Grigorescu, S.; Strasser, P.; Schmuki, P. *Chem. Mater.* **2015**, 27, 2360.
 - [12] Pandya, K.; O'grady, W.; Corrigan, D.; McBreen, J.; Hoffman, R. J. *Phy. Chem.* **1990**, 94, 21.
 - [13] Szytula, A.; Murasik, A.; Balanda, M. *Phys. Status Solidi B* **1971**, 43, 125.
 - [14] Gao, M.; Sheng, W.; Zhuang, Z.; Fang, Q.; Gu, S.; Jiang, J.; Yan, Y. *J. Am. Chem. Soc.* **2014**, 136, 7077.
 - [15] Tong, Y.; Xu, J.; Jiang, H.; Gao, F.; Lu, Q. *Chem. Eng. J.* **2017**, 316, 225.
 - [16] Luan, C.; Liu, G.; Liu, Y.; Yu, L.; Wang, Y.; Xiao, Y.; Qiao, H.; Dai, X.; Zhang, X. *ACS Nano* **2018**, 12, 3875.
 - [17] Jiang, J.; Sun, F.; Zhou, S.; Hu, W.; Zhang, H.; Dong, J.; Jiang, Z.; Zhao, J.; Li, J.; Yan, W. *Nat. Commun.* **2018**, 9, 2885.
 - [18] Chen, L.; Zhang, H.; Chen, L.; Wei, X.; Shi, J.; He, M. *J. Mater. Chem. A* **2017**, 5, 22568.
 - [19] Zhang, C.; Shao, M.; Zhou, L.; Li, Z.; Xiao, K.; Wei, M. *ACS Appl. Mater. Interfaces* **2016**, 8, 33697.
 - [20] Todoroki, N.; Wadayama, T. *ACS Appl. Mater. Interfaces* **2019**, 11, 47, 44161.
 - [21] Peng, C.; Ran, N.; Wan, G.; Zhao, W.; Kuang, Z.; Lu, Z.; Sun, C.; Liu, J.; Wang, L.; Chen, H. *ChemSusChem* **2019**, DOI: 10.1002/cssc.201902841.
 - [22] Dong, Y.; Komarneni, S.; Zhang, F.; Wang, N.; Terrones, M.; Hu, W.; Huang, W. *Appl. Catal. B: Environ.* **2019**, 118343.
 - [23] Lv, L.; Li, Z.; Ruan, Y.; Chang, Y.; Ao, X.; Li, J.-G.; Yang, Z.; Wang, C. *Electrochim. Acta* **2018**, 286, 172.
 - [24] Qiao, C.; Zhang, Y.; Zhu, Y.; Cao, C.; Bao, X.; Xu, J. *J. Mater. Chem. A* **2015**, 3, 6878.
 - [25] Zhou, Q.; Chen, Y.; Zhao, G.; Lin, Y.; Yu, Z.; Xu, X.; Wang, X.; Liu, H. K.; Sun, W.; Dou, S. X. *ACS Catal.* **2018**, 8, 5382.
 - [26] Li, J.; Lian, R.; Wang, J.; He, S.; Rui, Z. *Electrochim. Acta* **2019**, 135395.
 - [27] Zhao, J.; Wang, X.-r.; Chen, F.-w.; He, C.; Wang, X.-j.; Li, Y.-p.; Liu, R.-h.; Chen, X.-m.; Hao, Y.-j.; Yang, M. *Inorg. Chem. Front.* **2020**, 7, 737.
 - [28] Ye, C.; Wang, M.-Q.; Bao, S.-J.; Ye, C. *ACS Appl. Mater. Interfaces* **2019**, 11, 30887.
 - [29] Fan, K.; Chen, H.; Ji, Y.; Huang, H.; Claesson, P. M.; Daniel, Q.; Philippe, B.; Rensmo, H.; Li, F.; Luo, Y. *Nat. Commun.* **2016**, 7, 11981.
 - [30] Li, P.; Duan, X.; Kuang, Y.; Li, Y.; Zhang, G.; Liu, W.; Sun, X. *Adv. Energy Mater.* **2018**, 8, 1703341.
 - [31] Yang, Y.; Dang, L.; Shearer, M. J.; Sheng, H.; Li, W.; Chen, J.; Xiao, P.; Zhang, Y.; Hamers, R. J.; Jin, S. *Adv. Energy Mater.* **2018**, 8, 1703189.
 - [32] Xu, J.; Wang, M.; Yang, F.; Ju, X.; Jia, X. *Inorg. Chem.* **2019**, 58, 13037.
 - [33] Xu, H.; Wang, B.; Shan, C.; Xi, P.; Liu, W.; Tang, Y. *ACS Appl. Mater. Interfaces* **2018**, 10, 6336.
 - [34] Song, S.; Yu, L.; Hadjiev, V. G.; Zhang, W.; Wang, D.; Xiao, X.; Chen, S.; Zhang, Q.; Ren, Z. *ACS Appl. Mater. Interfaces* **2019**, 11, 32909.
 - [35] Long, J.; Yang, Z.; Huang, J.; Zeng, X. *J. Power Sources* **2017**, 359, 111.
 - [36] Chen, S.; Duan, J.; Jaroniec, M.; Qiao, S. Z. *Angew. Chem. Int. Ed.* **2013**, 52, 13567.
 - [37] Chen, R.; Sun, G.; Yang, C.; Zhang, L.; Miao, J.; Tao, H.; Yang, H.; Chen, J.; Chen, P.; Liu, B. *Nanoscale Horiz.* **2016**, 1, 156.
 - [38] Yin, S.; Tu, W.; Sheng, Y.; Du, Y.; Kraft, M.; Borgna, A.; Xu, R. *Adv. Mater.* **2018**, 30, 1705106.
 - [39] Yu, L.; Yang, J. F.; Guan, B. Y.; Lu, Y.; Lou, X. W. *Angew. Chem. Int. Ed.* **2018**, 57, 172.
 - [40] Zhang, J.; Liu, J.; Xi, L.; Yu, Y.; Chen, N.; Sun, S.; Wang, W.; Lange, K. M.; Zhang, B. *J. Am. Chem. Soc.* **2018**, 140, 3876.
 - [41] Zhu, W.; Liu, L.; Yue, Z.; Zhang, W.; Yue, X.; Wang, J.; Yu, S.; Wang, L.; Wang, J. *ACS Appl. Mater. Interfaces* **2017**, 9, 19807.
 - [42] Zhao, Z.; Wu, H.; He, H.; Xu, X.; Jin, Y. *Adv. Funct. Mater.* **2014**, 24, 4698.
 - [43] Wang, P.; Li, Y.; Li, S.; Liao, X.; Sun, S. *J. Mater. Sci.: Mater. Electron.* **2017**, 28, 9221.
 - [44] Duan, J.; Chen, S.; Zhao, C. *Nat. Commun.* **2017**, 8, 15341.
 - [45] Xu, J.; Zhao, Y.; Li, M.; Fan, G.; Yang, L.; Li, F. *Electrochim. Acta* **2019**, 307, 275.
 - [46] Zhang, W.-D.; Yu, H.; Li, T.; Hu, Q.-T.; Gong, Y.; Zhang, D.-Y.; Liu, Y.; Fu, Q.-T.; Zhu, H.-Y.; Yan, X. *App. Catal. B: Environ.* **2019**, 118532.
 - [47] Li, J.-G.; Sun, H.; Lv, L.; Li, Z.; Ao, X.; Xu, C.; Li, Y.; Wang, C. *ACS Appl. Mater. Interfaces* **2019**, 11, 8106.
 - [48] Lee, G.; Na, W.; Kim, J.; Lee, S.; Jang, J. *J. Mater. Chem. A* **2019**, 7, 17637.
 - [49] Chen, Z.; Ha, Y.; Jia, H.; Yan, X.; Chen, M.; Liu, M.; Wu, R. *Adv. Energy Mater.* **2019**, 9, 1803918.
 - [50] Wu, H.; Yin, K.; Qi, W.; Zhou, X.; He, J.; Li, J.; Liu, Y.; He, J.; Gong, S.; Li, Y. *ChemSusChem* **2019**, 12, 2773.
 - [51] Xie, J.; Zhang, X.; Zhang, H.; Zhang, J.; Li, S.; Wang, R.; Pan, B.; Xie, Y. *Adv. Mater.* **2017**, 29, 1604765.
 - [52] Xu, Z.; Fan, R.; Zhou, X.; Huang, G.; Wu, X.; Shen, M. *ACS Sustainable Chem. Eng.* **2019**, 7, 19832.
 - [53] Han, X.; Yu, C.; Zhou, S.; Zhao, C.; Huang, H.; Yang, J.; Liu, Z.; Zhao, J.; Qiu, J. *Adv. Energy Mater.* **2017**, 7, 1602148.
 - [54] Tang, C.; Zhang, R.; Lu, W.; He, L.; Jiang, X.; Asiri, A. M.; Sun, X. *Adv. Mater.* **2017**, 29, 1602441.
 - [55] Zhang, W.; Li, Y.; Zhou, L.; Zheng, Q.; Xie, F.; Lam, K. H.; Lin, D. *Electrochim. Acta* **2019**, 323, 134595.
 - [56] Zhang, B.; Lui, Y. H.; Ni, H.; Hu, S. *Nano Energy* **2017**, 38, 553.
 - [57] Xu, K.; Chen, P.; Li, X.; Tong, Y.; Ding, H.; Wu, X.; Chu, W.; Peng, Z.; Wu, C.; Xie, Y. *J. Am. Chem. Soc.* **2015**, 137, 4119.
 - [58] Jia, X.; Zhao, Y.; Chen, G.; Shang, L.; Shi, R.; Kang, X.; Waterhouse, G. I.; Wu, L. Z.; Tung, C. H.; Zhang, T. *Adv. Energy Mater.* **2016**, 6, 1502585.
 - [59] Zhang, B.; Xiao, C.; Xie, S.; Liang, J.; Chen, X.; Tang, Y. *Chem. Mater.* **2016**, 28, 6934.
 - [60] Ali, T.; Wang, X.; Tang, K.; Li, Q.; Sajjad, S.; Khan, S.; Farooqi, S. A.; Yan, C. *Electrochim. Acta* **2019**, 300, 45.
 - [61] Tang, C.; Cheng, N.; Pu, Z.; Xing, W.; Sun, X. *Angew. Chem. Int. Ed.* **2015**, 54, 9351.
 - [62] Jin, S. *ACS Energy Lett.* **2017**, 2, 1937.
 - [63] Xiong, P.; Zhang, X.; Wan, H.; Wang, S.; Zhao, Y.; Zhang, J.; Zhou, D.; Gao, W.; Ma, R.; Sasaki, T. *Nano Lett.* **2019**, 19, 4518.

Received January 7, 2020

Accepted February 6, 2020