Regulating $p$-block metals in perovskite nanodots for efficient electrocatalytic water oxidation

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Water oxidation represents the core process of many sustainable energy systems, such as fuel cells, rechargeable metal-air batteries, and water splitting. Material surface defects with high-energy hanging bonds possess superb intrinsic reactivity, whose actual performance is limited by the dimension and conductivity of the electrocatalyst. Herein we propose a surface defect-rich perovskite electrocatalyst through a $p$-block metal regulation concept to achieve high performance for oxygen evolution. As a typical $p$-metal, Sn$^{4+}$ dissolves from the solid phase from model SnNiFe perovskite nanodots, resulting in abundant surface defects with superior water oxidation performance. An oxygen pool model and a fusion-evolution mechanism are therefore proposed for the in-depth understanding of $p$-block metal regulation and the oxygen evolution reaction. The energy chemistry unveiled herein provides insights into water oxidation and helps to tackle critical issues in multi-electron oxygen electrocatalysis.
Electrocatalysis constitutes the core process of abundant sustainable energy systems such as fuel cells, rechargeable metal-air batteries, and water splitting. However, classical electrochemical reactions (for instance, oxygen evolution reaction (OER), oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), etc.) are very sluggish in kinetics and strongly inhibit the efficiency of the energy devices. Decades of researches have been carried out in exploring high-performance electrocatalysts, including noble metal compounds, transition metal hydrides, oxides, sulfides, perovskites, and their composites. Insights into the rational design of efficient electrocatalysts are strongly desired in this field in order to avoid tedious trial and error exploration.

The intrinsic reactivity, the amount of exposed active sites, and the electrical conductivity are the most significant aspects for a well-established electrocatalyst with excellent reactivity. It is widely accepted that surface defects possess high intrinsic reactivity toward electrocatalysis. The electrochemical reactions only happen at the surface of the electrocatalysts where feedstock/product can reach and electrons can be transferred during OER, ORR, and HER process. Surface defects with high-energy binding and dispersed empty electron orbitals are suitable for chemical adsorption and tend to interact strongly with reactants.

Perovskites are a family of defect-abundant materials and exhibit excellent OER activity comparable to that of precious metal oxides. In a typical perovskite, A sites are usually alkaline earth metals, rare earth metals, or p-block metals while B sites are occupied with transition metals. Both A sites and B sites are relatively easily substituted or dissociated, which usually results in an oxygen non-stoichiometry and thus oxygen deficiency. Such oxygen deficiency provides abundant surface defects, which are believed to be the active sites for OER. Meanwhile, the concept of nano-structured electrocatalysts affords high surface area and abundant active sites exposed to feedstocks, and is therefore highly expected to promote the overall electrochemical performance. A stable conductive framework is also strongly considered to guarantee full demonstration of the intrinsic reactivity of electrocatalysts by reducing the resistance of electron transportation not only at the reactive interface, but also between the electrocatalysts and the current collectors.

Based on this consideration, we introduced a unique strategy of p-block metal regulation of nano-sized perovskite electrocatalysts for OER. P-block metals possess a dual nature of metallicity and non-metallicity due to their unfilled d orbitals. In a certain alkaline condition, p-block metal ions precipitate to form crystallized hydroxides appearing as a typical metal element. When the condition changes through the rise of alkalinity or addition of extra ligands, the p-block metal ions dissociate from the solid phase as soluble coordination complexes because of their non-metallicity, resulting in abundant vacant sites at the surface. Utilizing such unique properties of p-block metals, we can construct in situ defects with high intrinsic reactivity at the surface of perovskite electrocatalysts.

Results

Material synthesis and characterization. To prove the concept, Sn is selected as a typical p-block metal to regulate SnNiFe perovskite hydroxide nanodots in situ hybridized with mesoporous graphene framework (MGF). Ni²⁺, Fe³⁺, and Sn⁴⁺ co-precipitate into crystallized perovskite hydroxides spatially confined within the mesopores of graphene, exhibiting the structure of SnNiFe perovskite nanodots strongly coupled with graphene framework. As illustrated in Fig. 1, Sn⁴⁺ dissociates from the perovskite host and leaves in situ vacant sites at the surface during the p-block metal regulated electrochemical activation. The loss of Sn⁴⁺ affords abundant surface defects with high reactivity and facilitates the oxidation of transition metal ions into higher oxidative states at the same time, which are considered as critical active species toward OER. The activated electrocatalyst exhibits efficient OER performance, superior to the state-of-art OER electrocatalyst IrO₂ in aspects of reactivity, kinetics, and durability.

The conductive MGF support was fabricated by a templated chemical vapor deposition (CVD) method. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images demonstrate a hierarchical structure of MGF with plentiful mesopores with a uniform diameter within 10 nm. The hybrid electrocatalyst of SnNiFe perovskite hydroxide nanodots with MGF (named as n-SnNiFe) was synthesized by in situ co-precipitation. No bulk perovskite is observed at macro-scale morphology characterization (Supplementary Fig. 2). High angle annular dark field scanning TEM (HAADF-STEM) image in Fig. 2b exhibits the uniform distribution of perovskite nanodots in 3D graphene scaffolds. Further morphology characterization indicates the SnNiFe perovskite is spatially confined within the mesopores of MGF (Fig. 2c), resulting in SnNiFe nanodots with an average diameter of ca. 5 nm (Fig. 2c, inserted). The as-synthesized perovskite nanodots are well crystallized, which were proved by high-resolution TEM (Fig. 2d) and X-ray diffraction (XRD) patterns (Fig. 2e). The lattice fringes observed in Fig. 2d are identified to be (2 2 0), with the interplanar spacing being 0.269 nm.

Energy-disperse X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma optical emission spectrometer (ICP) were carried out for element analysis. The atomic ratio of Sn:(NiFe) of n-SnNiFe is close to 1 and Ni:Fe around 3.0 (Supplementary Fig. 3; Supplementary Table 1). The composition of n-SnNiFe is consistent with the theoretical stoichiometric ratio identified by comprehensive characterization. EDS mapping exhibits the uniform distribution of every element (Supplementary Fig. 4). The successful fabrication of n-SnNiFe perovskites attributes from the metallicity of transition metal and p-block metal. The n-SnNiFe with the structure of perovskite nanodots hybridized with conductive
MGF is expected to fully demonstrate the intrinsic OER reactivity of the electrocatalyst.

P-block metal activation and electrochemical evaluation. In order to create surface defects with intrinsic reactivity, p-block metal-regulated electrochemical activation of n-SnNiFe perovskite nanodots was performed. n-SnNiFe was electrochemically activated at a constant potential required to reach an initial current density of 5.0 mA cm$^{-2}$ in O$_2$-saturated 0.10 M KOH for 300 s. The p-block metal regulated n-SnNiFe electrocatalyst after electrochemical activation is named as p-SnNiFe.

During the electrochemical activation, an obvious activation current was observed (Fig. 3a) with the current density raising from 4.3 to 4.5 mA cm$^{-2}$. Figure 3b demonstrates the 95% $iR$-compensated linear sweep voltammetry (LSV) profiles at a scan rate of 10.0 mV s$^{-1}$. The current density of p-NiFeSn perovskite electrocatalyst is distinctly increased compared with non-activated n-SnNiFe perovskite nanodots. The overpotential of p-SnNiFe at a current density of 10.0 mA cm$^{-2}$ is 350 mV, which is among the best OER electrocatalysts (Supplementary Table 2) and even 20 mV better than IrO$_2$, which is recognized as the state-of-the-art OER electrocatalyst.

Tafel plots (Fig. 3c) exhibit the superiority of p-SnNiFe perovskites (35.0 mV dec$^{-1}$) over both n-SnNiFe perovskites (45.9 mV dec$^{-1}$) and IrO$_2$ (134 mV dec$^{-1}$) with regard to OER kinetics. The stability of the electrocatalysts was characterized by a chronoamperometric method with an initial current density of 10.0 mA cm$^{-2}$. The current density of p-SnNiFe retains 60% after 20,000 s test while only 40% of the current density of IrO$_2$ is preserved, indicating better stability of p-SnNiFe perovskites against OER (Fig. 3d).

Bulk SnNiFe perovskite particles (named as b-SnNiFe) and the mechanical mixture of b-SnNiFe and MGF (named as b-SnNiFe + MGF) were prepared as control samples to demonstrate the significance of the unique pomegranate-like nanostructure of specially confined perovskites and highly conductive MGF toward both electrochemical activation and OER performance. The b-SnNiFe perovskite electrocatalyst exhibits a morphology of aggregated massive particles with an average diameter around 200 nm (Supplementary Fig. 5). The XRD patterns are identical with n-SnNiFe perovskites (Supplementary Fig. 6), along with similar stoichiometric ratio of Sn, Ni, and Fe (Supplementary Fig. 7; Supplementary Table 1) and element distribution (Supplementary Fig. 8), indicating the smart in situ hybridized design with MGF contributes to the fabrication of nano structures without interfering the nature of SnNiFe perovskites. Bulk SnNiFe perovskite particles share identical chemical constitution and structure with n-SnNiFe, and are only different in morphology of perovskite and existence of MGF, making ready for illustration of the necessity of pomegranate-like nanostructures with nano-sized perovskites and highly conductive graphene toward effective electrocatalysis.

The electrochemical activation process of b-SnNiFe and b-SnNiFe + MGF was similar to that of n-SnNiFe perovskites, and the p-block metal regulated samples after activation are named as pb-SnNiFe and pb-SnNiFe + MGF, respectively. The OER reactivity of b-SnNiFe and b-SnNiFe + MGF electrocatalysts was enhanced, which was suggested by the raised current density during in situ electrochemical activation and decreased overpotential (Supplementary Figs. 9, 10). For instance, the overpotential at 10.0 mA cm$^{-2}$ was 20 mV decreased after electrochemical activation for b-SnNiFe + MGF. The improvement of OER reactivity indicates the universality of the p-block metal regulation strategy. However, the OER performance of neither pb-SnNiFe nor pb-SnNiFe + MGF is comparable with p-SnNiFe. The overpotential at 10.0 mA cm$^{-2}$ of p-SnNiFe is 110 mV lower than that of pb-SnNiFe + MGF and far lower than pb-SnNiFe. In addition, the Tafel slope decreases from 190 mV dec$^{-1}$ for pb-SnNiFe, 59.6 mV dec$^{-1}$ for pb-SnNiFe + MGF to 35.0 mV dec$^{-1}$ for p-SnNiFe (Supplementary Fig. 11). These evidences strongly confirm the superiority of p-SnNiFe in OER reactivity and kinetics.

In order to evaluate the stability of SnNiFe perovskite hydroxides, long-time durability tests were performed on b-SnNiFe. Carbon nanotube (CNT, with a mass ratio of 20%) was added to ensure the conductivity and the sample is named as...
b-SnNiFe + CNT. As is shown in Supplementary Fig. 12, the OER reactivity of b-SnNiFe + CNT electrocatalyst remains stable, with the overpotential at 10 mA cm\(^{-2}\) increases only 20 mV after 10,000 s, 25 mV after 20,000 s, and 42 mV after 40,000 s durability tests. The Tafel slopes exhibit similar tendency with slight increases. XRD patterns in Supplementary Fig. 13 and TEM images in Supplementary Fig. 14 further indicate the structure and morphology stability of perovskite hydroxides. The SnNiFe perovskite hydroxides exhibit satisfactory structural and electrochemical stability under OER condition in alkaline solution.

To further identify the origin of superiority of p-SnNiFe over pb-SnNiFe and pb-SnNiFe + MGF, electrochemical impedance spectroscopy (EIS) and electrochemical active surface area (ECSA) analysis were carried out. The electrical conductivity of nano-sized SnNiFe perovskites in situ hybridized with MGF is better for both pristine and electrochemical activated
During the activation as illustrated in Supplementary Fig. 15. In addition, MGF contributes to the promotion of ECSA exhibited in Supplementary Fig. 16, which is characterized by the double-layer capacity. Considering the ability of electrochemical activation and OER performance, the nano-sized perovskite and conductive framework play a critical role to enhance the OER performance for SnNiFe perovskites. The rational design of nanostructure and hybridization with conductive framework is of great significance for a well-established electrocatalyst.

Mechanism of p-block metal regulation. In order to verify the surface defects attributed to Sn loss and understand the mechanism of p-block metal regulation of n-SnNiFe perovskites, detailed characterization of activated p-SnNiFe perovskites was carried out. The s-SnNiFe perovskite was prepared by soaking n-SnNiFe perovskite in the electrolyte as a control sample. There is no significant change between p-SnNiFe and s-SnNiFe in either morphology or crystal structure as shown in Fig. 4a, Supplementary Figs. 17, 18, suggesting morphology is not the key factor leading to OER activation. In addition, neither the electrical conductivity nor the surface hydrophilicity of the electrocatalysts is relevant confirmed by EIS in Supplementary Fig. 19 and Supplementary Table 3 and contact angel in Supplementary Fig. 20, respectively. However, element analysis exhibits consistent results of Sn loss by EDS, XPS, and ICP analysis (Supplementary Figs. 21, 22, and Supplementary Table 1). The atomic ratio of Sn:(NiFe) decreases from ~0.9 of n-SnNiFe and s-SnNiFe to ~0.7 of p-SnNiFe (Fig. 4b), with the atomic ratio of Ni:Fe remains relative stable around 3 (Supplementary Fig. 23). The dissociation of Sn lefts abundant vacant sites, which is confirmed by enhanced ECSA of p-SnNiFe measured by capacitive current caused by adsorption and desorption of electrolyte (Fig. 4c).

Meanwhile, with the loss of positively charged Sn⁴⁺, transition metal ions in solid perovskite phase feel a stronger positive electric field. The transition metal ions tend to lose electron and therefore be oxidized to higher oxidative states. As shown in Fig. 4d, the high-resolution Ni 2p XPS spectra of p-SnNiFe exhibit a 0.60 eV shift to higher binding energy compared with n-SnNiFe and s-SnNiFe perovskites sharing similar Ni 2p XPS spectra. Such results strongly indicate the oxidation process and higher oxidative state of Ni in p-SnNiFe perovskites, which is considered to contribute to the enhanced OER performance. In contrast, the oxidative states of Fe³⁺ and Sn⁴⁺ remain relative stable during the activation as illustrated in Supplementary Fig. 24 by XPS Fe 2p spectra and Sn 3p spectra. Above all, the unique dual properties of metallicity and non-metallicity of Sn is the main factor for construction of surface defects and oxidation of active transition metal ions, resulting in improved electrocatalysts and excellent OER performance.

Methods

Synthesis of MGF. MGF was prepared through a CVD method using mesoporous MgO as template and CH₄/NH₃ as carbon/nitrogen source, respectively. The MgO template was synthesized by a facile hydrothermal reaction using commercial MgO. Typically, 2.20 g polyethylene glycol (PEG)-2000 was dissolved in 100 mL deionized water and 1.0 g MgO was added. The slurry was stirred for 48 h and then transferred into a 200 mL Teflon autoclave for hydrothermal reaction at 200 °C for 48 h. The precipitate was filtered, washed with deionized water for three times and dried at 80 °C overnight. The mesoporous MgO template was obtained after calcination of the as-obtained precursor at 650 °C for 5.0 h. The CVD growth was carried out in a furnace with MgO template placed in the middle of a horizontal quartz tube. The reactor was heated to 950 °C under Ar flow (150 mL min⁻¹) with a heating rate of 20 °C min⁻¹. Both CH₄ (70 mL min⁻¹) and NH₃ (30 mL min⁻¹) were simultaneously introduced into the reactor for 15 min after the temperature was stable, and then the furnace was cooled naturally to room temperature under Ar protection. The product was purified using 6.0 mol L⁻¹ HCl at 95 °C for 12 h to fully remove the MgO template. After filtering, washing with deionized water and ethanol, and freeze-drying for 24 h, MGF was obtained for further synthesis.

Synthesis of perovskite electrocatalysts. n-SnNiFe was synthesized by in situ co-precipitation. About 100 mg MgO was dispersed into 30 mL N-methylpyrrolidone (NMP) under sonication for 30 min to form a homogeneous suspension. About 1.5 mmol Ni(NO₃)₂·6H₂O, 0.50 mmol Fe(NO₃)₃·9H₂O, and 2.0 mmol citric acid were dissolved in 50 mL deionized water under stirring for 10 min and then mixed with the MgO slurry. About 10 mL SnCl₂ aqueous solution (0.2 mol L⁻¹) was added into the above mixture under vigorous stirring. After that, 1.0 mol L⁻¹ NaOH was added dropwise into the as-obtained solution under sonication until the pH reached 10. The sonication went for another 30 min to accelerate the precipitation reaction. The product was separated by centrifuging at 10,000 rpm for 10 min and purified by washing with deionized water and ethanol for three times, respectively. The n-SnNiFe was finally obtained after freeze-drying for 24 h. b-SnNiFe was synthesized by under otherwise identical conditions without MGF. b-SnNiFe + MGF was prepared by simply mixing b-SnNiFe and MgO under grind.

Electrochemical activation of perovskite electrocatalysts. The electrochemical activation process was carried out using a three-electrode system. The samples for activation were prepared using the same method as the working electrode fabrication for electrochemical measurements. The activation conditions were identical with electrochemical evaluation process, with the electrolyte to be O₂-saturated 0.10 M KOH (see more details in the electrolysis section). All
samples were electrochemically activated at a constant potential required to reach a specified initial current density for 300 s. n-SnNiFe and b-SnNiFe + MgF were activated at electrode current density of 5 mA cm$^{-2}$, resulting in p-SnNiFe and p-b-SnNiFe + MgF, respectively. The initial current density of b-SnNiFe was determined to be 2.5 mA cm$^{-2}$ due to its poor reactivity and the final product was p-b-SnNiFe. s-SnNiFe was prepared as control sample by simply soaking n-SnNiFe into the electrolyte for 300 s.

**Characterization.** The morphology was characterized using a JSM 7401F (JEOL Ltd., Tokyo, Japan) SEM at 3.0 kV and a JEM 2010 (JEOL Ltd.) TEM at 120.0 kV. EDS analysis and mapping were performed using the JEM 2010 TEM equipped with an Oxford Instrument energy dispersive X-ray spectrometer. High-resolution transmission electron microscope (HRTEM) images were recorded using a JEOL Tecnai 720 T E F20 microscope operated at 120 kV and 120 mA. XRD was carried out by Escalab 250xi, with all XPS spectra corrected using C 1s line at 284.6 eV. Elemental analysis was performed using an inductively coupled plasma optical emission spectrometer (IRIS Intrepid II XSP, ThermoFisher, USA). The contact angle was measured using an OCA2000 Optical contact angle measuring instrument (Dataphysics, Germany).

**Electrocatalysis.** Electrochemical measurements were performed using a three-electrode system controlled by a CHI 760D electrochemistry station (CH Instrument, USA). A platinum sheet electrode served as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was a rotating disk electrode with a disk diameter of 5 mm. All electrochemical measurements were carried out in O$_2$-saturated 0.1 M K$_2$SO$_4$ solution at 298 K. All electrochemical measurements were carried out by LSV using a Platinum Working electrode, a Platinum Counter electrode, and a Ag/AgCl Reference electrode, respectively.

**Electrocatalytic activity.** The electrocatalyst was dispersed in 0.95 mL ethanol and 0.05 mL Na$_2$SO$_4$ solution to form a homogeneous suspension. The working electrode was fabricated using the following method: 5.0 mg electrocatalyst was dispersed in 0.95 mL ethanol and 0.05 mL Na$_2$SO$_4$ solution and the suspension was dropped onto the glass carbon disk electrode, which was polished in advance. The working electrode was ready for electrochemical measurements.

**Electrochemical characterization.** Electrochemical measurements were performed using a three-electrode system controlled by a CHI 760D electrochemistry station (CH Instrument, USA). A platinum sheet electrode served as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was a rotating disk electrode with a disk diameter of 5 mm. All electrochemical measurements were carried out in O$_2$-saturated 0.1 M K$_2$SO$_4$ solution at 298 K. All electrochemical measurements were carried out by LSV using a Platinum Working electrode, a Platinum Counter electrode, and a Ag/AgCl Reference electrode, respectively.

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Author contributions
Q.Z. conceived the study and supervised the work. Q.Z. and B.-Q.L. designed the experiments. B.-Q.L. and Z.-J.X. synthesized the electrocatalysts and evaluated the water oxidation performance. B.Z. carried out TEM analysis, C.T. and H.-F.W. carried out structural and composition analysis of the electrocatalyst. B.-Q.L. and Q.Z. wrote the paper. All authors contributed to the discussion.

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