Operando Unraveling Photothermal-Promoted Dynamic Active Sites Generation in Spinel NiFe$_2$O$_4$ for Oxygen Evolution

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Abstract

The ability to develop highly active and low-cost electrocatalysts represents an important endeavor toward accelerating sluggish water-oxidation kinetics. Herein, we report, for the first time, the implementation and unravelling of photothermal effect of spinel nanoparticles (NPs) on promoting dynamic active sites generation to markedly enhance their oxygen evolution reaction (OER) activity via an integrated operando Raman and density functional theory (DFT) study. Specifically, NiFe2O4 (NFO) NPs are first synthesized by capitalizing on amphiphilic star-like diblock copolymers as nanoreactors. Upon the NIR light irradiation, the photothermal heating of the NFO-based electrode progressively raises the temperature, accompanied by a marked decrease of overpotential. Accordingly, only an overpotential of 309 mV is required to yield a high current density of 100 mA cm⁻², greatly lower than recently-reported earth-abundant electrocatalysts. More importantly, photothermal effect of NFO NPs not only significantly reduces the activation energy necessitated for water splitting, but also facilitates surface reconstruction into high-active oxyhydroxides at lower potential (1.36 V) under OER conditions, as revealed by operando Raman spectra-electrochemistry. Moreover, the DFT calculation corroborates that these reconstructed (Ni,Fe)oxyhydroxides are electrocatalytically active sites as the kinetics barrier is largely reduced over pure NFO without surface reconstruction. Given the diversity of materials (metal oxides, sulfides, phosphides, etc.) possessing the photo-to-thermal conversion, this effect may thus provide a unique and robust platform to boost highly-active surface species in nanomaterials for fundamental understanding of enhanced performance that may underpin future advances in electrocatalysis, photocatalysis, solar energy conversion and renewable energy production.

Introduction

Motivated by the need for accelerating sluggish reaction kinetics at the anode,[1, 2] the focus of water electrolysis has been centered heavily on oxygen evolution reaction (OER) towards sustainable hydrogen fuel production. To date, there has been much effort in developing low-cost yet high-performance earth-abundant transition-metal alternatives to commonly used noble metals for OER. Intriguingly, many Ni-, Co-, Fe- and Mn-based oxides experience dynamic surface-reconstruction process to form more active oxyhydroxides, which are recognized as true catalytically active species for OER in alkaline media.[3, 4] Among various transition-metal-based OER catalysts, bimetal spinel-structured oxides in the form of AB₂O₄ (A and B are different metal ions) have garnered much attention due to their rich compositions, electron configurations and valence states.[5] Interestingly, inverse spinel NiFe₂O₄ (NFO), in principle, exhibits enhanced catalytic activity toward OER because of the presence of multivalent elements (i.e., Ni³⁺/Ni²⁺ and Fe³⁺/Fe²⁺).[6] It is important to note that studies on facilitating the surface reconstruction of NFO to achieve high-performance OER are relatively few, and fundamental understanding as to what makes the derived OER catalysts perform well remains elusive.

Recently, introducing thermal energy to promote electrocatalytic conversion has attracted significant interest.[7] Clearly, the use of thermal energy would reduce the activation energy of water oxidation and
thus accelerate the electrocatalytic kinetics, thereby leading to improved efficiency. Electrocatalysts with photothermal effect (referred to as photothermal electrocatalysts) enable in-situ heating due to photo-thermal conversion under the illumination with visible or near infrared (NIR) light, thereby dispensing with the need for extra devices required to provide thermal energy. More importantly, in sharp contrast to common approaches where the entire solution is heated, the photothermal effect is localized on electrocatalysts themselves,\(^8\) thus effectively enabling heat modulation to a defined region (i.e., the working electrode). Despite recent impressive advances in transition metal oxides (e.g., Fe\(_3\)O\(_4\) and Co\(_3\)O\(_4\)) as photothermal agents for cancer therapy,\(^8\) their implementations for photothermal-assisted OER, in particular spinel oxides, are comparatively few and limited in scope. Moreover, it has been reported that Ni- and Co-based OER catalysts are prone to surface reconstruction into highly active oxyhydroxides.\(^9,10\) Surprisingly, the photothermal effect on promoting surface reconstruction in spinel oxide catalysts has yet to be explored.

Herein, we report, for the first time, an integrated operando Raman and density functional theory plus Hubbard U (DFT + U) study to exercise and unveil the photo-to-thermal conversion of inverse spinel oxide nanoparticles (NPs) in promoting the generation of dynamic active sites via surface reconstruction into oxyhydroxides and thus greatly enhancing their OER activity. First, a series of amphiphilic star-like poly(acrylic acid)-block-poly(styrene-co-acrylonitrile) (denoted PAA-b-PSAN) diblock copolymers with well-defined molecular weight (MW) and low polydispersity index (PDI) are exploited as nanoreactors to synthesize a set of PSAN-ligated NFO NPs with different sizes and PSAN chain lengths. The effects of the NFO NP sizes and the outer PSAN chain lengths on catalytic activity of NFO NPs are then scrutinized. Interestingly, NFO NPs of largest size (~12 nm) ligated with shortest PSAN chains (MW = 7K) display the best OER reactivity on glassy carbon electrode in alkaline media as a result of a high fraction of exposed electrochemically active surface area and fastest electrocatalytic kinetics. Subsequently, the photothermal effect of PSAN-ligated NFO NPs is exploited to promote their surface reconstruction and thus boost OER. Significantly, the reaction kinetics of OER is found to be considerably improved due to the lowered activation energy \(E_a\), as modulated by the thermal energy originated from photothermal conversion of NFO. More importantly, operando Raman spectra-electrochemistry study is performed to unveil the mechanism of photothermal-assisted enhancement in OER reaction, revealing the emergence of electrocatalytically active \(\gamma\)-NiOOH at lower potential (1.36 V) during the surface reconstruction process with photothermal effect. Finally, the first-principle calculations substantiate that the reconstructed surface (i.e., (Ni,Fe)oxyhydroxides) plays a pivotal role as active site for electrocatalytic reaction. As such, photothermal electrocatalysts (e.g., metal oxides, sulfides, phosphides, etc.) may render significantly low overpotential and fast OER kinetics, representing an array of important materials that couple the localized heating with electrochemistry for effectively producing renewable energy production.

**Results**

**Synthesis and characterization of PSAN-ligated NiFe\(_2\)O\(_4\) nanoparticles.** Fig. 1 depicts the synthetic route to hairy PSAN-ligated NFO NP by employing amphiphilic unimolecular star-like PAA-b-PSAN diblock...
copolymer as nanoreactor (see Experimental Section in Supplementary Information). First, a set of star-like poly(tert-butyl acrylate)-block-poly(styrene-co-acrylonitrile) (denoted PtBA-b-PSAN; upper right panel in Fig. 1) diblock copolymers with controlled yet tunable MWs and low PDI of both blocks is synthesized via atom transfer radical polymerization (ATRP) of tert-butyl acrylate (tBA) monomers, followed by styrene and acrylonitrile co-monomers, using heptakis[2,3,6-tri-O-(2-bromo-2-methylpropionyl)]-β-cyclodextrin (21Br-β-CD) as a macroinitiator.\textsuperscript{11,12} Subsequently, the inner PtBA blocks are hydrolyzed into PAA blocks, resulting in amphiphilic star-like PAA-b-PSAN (lower right panel; Fig. 1) (Experimental Section). It is worth noting that, in contrast to conventional micelles formed by linear amphiphilic block copolymer counterpart,\textsuperscript{13} in the present study each PAA-b-PSAN arm in star-like diblock copolymer covalently anchored to the 21-Br-β-CD core are capable of maintaining a much more structurally stable spherical macromolecular architecture.

The as-prepared amphiphilic star-like PAA-b-PSAN diblock copolymers are then utilized as nanoreactors to direct the growth of NFO NPs ligated by the outer hydrophobic PSAN chains that are originally covalently connected to the inner hydrophilic PAA chains. The reaction is performed in the mixed solvent of diphenyl ether/benzyl alcohol (DPE/BA at a 9:1 ratio by volume) (see Experimental Section). First, the unimolecular micelles of amphiphilic star-like PAA-b-PSAN are dissolved in DPE with a shrunk PAA core as DPE is a good solvent for PSAN blocks yet poor solvent for PAA blocks. The NFO precursors (Ni(OAc)\textsubscript{2} and Fe(AcAc)\textsubscript{3}) are added to the star-like PAA-b-PSAN DPE solution under stirring. In order to expand the inner PAA chains to allow more precursor loading as well as improve NP morphology, BA is added to swell the inner compartment occupied by PAA chains as it is a good solvent for PAA yet poor solvent for PSAN. It is notable that due to the strong coordination interaction between PAA blocks and metal moieties of precursors, as well as the polar affinity of precursors to BA, the precursors accumulate within the PAA compartment, thereby effectively yielding PSAN-ligated NFO NPs at 250 °C (lower left panel; Fig. 1). Due to the living polymerization characteristic of ATRP, polymers with well-defined MWs and low PDI can be readily synthesized. Thus, the lengths of PAA and PSAN blocks in star-like PAA-b-PSAN can be controlled by varying the ATRP times of tBA (hydrolyzed from PtBA block into PAA block later) and SAN co-monomers, respectively,\textsuperscript{14} which in turn dictate the size of formed NFO NPs templated by the inner PAA blocks and the length of the outer PSAN chains. The MWs of star-like PtBA homopolymers and PtBA-b-PSAN and PAA-b-PASN (both inner PAA and outer PSAN blocks) diblock copolymers as well as the corresponding sizes of PSAN-ligated NFO NPs are summarized in Supplementary Table 1 (Supplementary Information).

Fig. 2 shows the representative transmission electron microscope (TEM) images of a set of PSAN-ligated NFO NPs of different sizes. Their average diameters are 3.3 ± 1.7 nm, 7.0 ± 1.8 nm, 12.0 ± 2.1 nm, and 12.1 ± 2.5 nm, respectively (denoted NFO-3-8K, NFO-7-15K, NFO-12-21K and NFO-12-7K in Supplementary Table 1, where the first and second numbers refer to the size of NP and MW of PSAN chain, respectively; Supplementary Information), template-grown by using the four star-like PAA-b-PSAN diblock copolymers with different MWs of inner PAA and outer PSAN blocks as nanoreactors. The size distribution histograms for PSAN-ligated NFO NPs are shown in Supplementary Fig. 1. Compared with the sizes of
the corresponding star-like PAA-b-PSAN nanoreactors in dimethylformamide (DMF) measured by dynamic light scattering (DLS; Supplementary Fig. 2 and Supplementary Table 1), a decrease in sizes of the resulting NPs may be ascribed to the use of 9/1 volume ratio of DPE/BA in the reaction and the shrinking of the PAA blocks during the crystallization process of NPs. In addition to interrogate the size effect of PSAN-ligated NFO NPs on the electrocatalysis performance, the NPs with the same size yet different length of outer hydrophobic PSAN chains are synthesized (i.e., NFO-12-7K and NFO-12-21K in Supplementary Table 1; 12-nm NPs with 7K and 21K MW of PSAN chains, respectively). Interestingly, the TEM sample of PSAN-ligated NFO-12-7K exposed to RuO$_4$ vapor$^{[15]}$ that preferentially stains the PSAN chains, yielding a grey shell situated on the surface of dark NFO NPs (Fig. 2e; also see the inset), signifying the PSAN chains are intimately and permanently ligated on the NP surface.

Typical X-ray diffraction (XRD) pattern of PSAN-ligated NFO NPs are shown in Supplementary Fig. 3. The peaks from PSAN-ligated NFO NPs at scattering angle 2θ of 30.3°, 35.7°, 43.4°, 53.8°, 57.4°, and 62.9° correspond to the diffraction from the (220), (311), (400), (422), (511), and (440) crystal planes of NFO (JCPDS Card No. 10-0325), respectively,$^{[16]}$ clearly suggesting that NFO NPs formed by the nanoreactor strategy are crystalline. The high-resolution TEM (HRTEM) image of NFO-12-7K (Fig. 2f) further reveals that the high-quality NPs with a lattice spacing of 0.25 nm corresponding to the (311) plane of NFO. Moreover, the HRTEM studies of NFO-3-8K, NFO-7-15K and NFO-12-21K (Supplementary Fig. 4a-c) demonstrate that PSAN-ligated NFO NPs of different sizes are also crystalline.

**The effects of the NP size and the PSAN chain lengths of PSAN-ligated NiFe$_2$O$_4$ NPs on oxygen evolution reaction performance.** We note that in order to prepare high-quality electrocatalyst ink mixed with carbon black, PSAN-ligated NFO NPs (e.g., NFO-12-7K) after washed with ethanol for several times (i.e., without subsequent drying; see Experimental Section) were directly added to DMF after synthesis. As a result, NPs were found to uniformly distribute on carbon black, and no residual NPs deposited outside carbon black substrate (Supplementary Fig. 5-6), suggesting their excellent dispersibility and contact with carbon black and thus ensuring a better conductivity of the electrocatalyst ink. Nonetheless, Fig. 3a compares linear sweep voltammetry (LSV) curves of four PSAN-ligated NFO NPs electrocatalysts, from which the effects of the NP size and the length of surface PSAN chains can be scrutinized. The template-grown NFO NPs displayed clear decreases in overpotential and onset potential with increasing NP size. Notably, NFO-12-7K NPs with the largest size (~12 nm) and the shortest PSAN chain (MW = 7K) manifested the lowest overpotential ($\eta_{20} = 329$ mV) at a current density of 20 mA cm$^{-2}$ and the lowest onset potential (266 mV), accordingly the highest catalytic activity because of its largest exposed active surface area, as verified by the electrochemical active surface area (ECSA, Supplementary Fig. 7), which was measured based on the double-layer capacitance ($C_{dl}$) of samples.$^{[17]}$ As shown in Fig. 3b, the $C_{dl}$ of NFO-12-7K is 830 µF cm$^{-2}$, which is the highest among all PSAN-ligated NFO NPs electrocatalysts. Taken together, NFO-12-7K NPs expose a highest density of active sites to the electrolyte during OER.

The OER kinetics of these PSAN-ligated NFO NP samples were further evaluated by Tafel plots. Fig. 3c shows the Tafel slopes of 130, 79, 59 and 40 mV dec$^{-1}$ for NFO-3-8K, NFO-7-15K, NFO-12-21K and NFO-
12-7K, respectively. The as-synthesized NFO-12-7K (i.e., 12 nm NP size ligated with 7K PSAN chains) exhibits the smallest Tafel slope, representing the most efficient electrocatalysts among the four samples and demonstrating the synergy of largest NP size with shortest outer PSAN chain in enhancing the OER activity. Overall, PSAN-ligated NFO-12-7K NPs outperformed the other samples in the four key metrics, as depicted in the histogram (Fig. 3d).

The conductivity of the samples was measured by EIS (Supplementary Fig. 8). The NFO-12-7K sample displayed a smallest charge transfer resistance ($R_{ct}$, the radius of semicircle in the low-frequency range), which is indicative of a fastest electrocatalytic kinetics.[18] Additionally, the semicircular radii of the samples in the EIS plot progressively decreased with the increasing NP size ligated with shorter outer PSAN chains. This is due to the faster electron transfer rate because of the larger exposed active surface area (as substantiated by $C_{dl}$ results in Supplementary Fig. 7), thereby offering the greater accessibility of ions to the exposed surface area. Moreover, it has been reported that oxygen vacancies can offer the substantially enhanced electrical conductivity because the delocalized electrons around an oxygen vacancy can be easily excited to the conduction band, thus enhancing the conductivity of catalyst.[19] It is notable that the relative peak intensity of oxygen vacancies (531.5 eV) to that of metal-O (530.1 eV) in the O 1s region (Supplementary Fig. 9a) exhibited a significant increase from NFO-3-8K to NFO-12-7K, indicating that PSAN-ligated NFO NPs with the largest NP size (12 nm) and the shortest surface PSAN chains (MW = 7K) (i.e., NFO-12-7K) possessed more oxygen vacancies. Therefore, the richest oxygen vacancies of NFO-12-7K may also contribute to the fastest electron transfer (smallest $R_{ct}$).

Supplementary Fig. 10 depicts a schematic to further elaborate the NP size effect on electrocatalytic activity of PSAN-ligated NFO NPs. As the electrolyte (1.0 M KOH solution) is a non-solvent for PSAN, the intimately and permanently ligated PSAN chains on the surface of NFO NP would collapse due to unfavorable interaction between PSAN and water. Such condensed PSAN chains form a hydrophobic shell covering a portion of NFO NPs surface, thus partially shielding the active surface area and in turn suppressing the OER activity to some extent. As shown in Supplementary Fig. 10a, for NFO NPs ligated with nearly the same length of PSAN chains (8K for NFO-3-8K, and 7K for NFO-12-7K), NFO-3-8K with a smaller nanoparticle size (3.3 ± 1.7 nm) than NFO-12-7K (12.1 ± 2.5 nm) is further adequately covered by PSAN chains, resulting in less active surface area exposed. Similarly, with the same NFO NP size (12.0 ± 2.1 nm for NFO-12-21K, and 12.1 ± 2.5 nm for NFO-12-7K), the longer PSAN chains (21K in NFO-12-21K compared to 7K in NFO-12-7K) impart denser PSAN shell situated on the NFO NP surface and thus further effectively block the electrolyte penetration through the shell, leading to a decreased active surface area during the OER process. Consequently, it is not surprising when placing the PSAN-ligated NFO NPs in KOH, compared to NFO-12-7K NPs, NFO-3-8K NPs delivered a lowest OER performance due to the least accessible active surface area that prevents the effective electrolyte ions (OH$^-$) transport (left panel; Supplementary Fig. 10b). Likewise, among all samples, NFO-12-7K least shielded by the PSAN shell would be most readily accessed by OH$^-$ ions (right panel; Supplementary Fig. 10b), thereby achieving the highest ECSA and lowest overpotential.
It is also notable that two control samples (i.e., NFO NPs synthesized by using star-like PAA homopolymers as template and no template, respectively) displayed poor OER activity because of the aggregation of NPs (Supplementary Fig. 11-12), further substantiating the importance of the presence of PSAN hairs on the NFO NP surface. Moreover, the LSV curve of pure star-like PAA-b-PSAN templates signified the negligible effect of polymers (either PSAN or PAA) on OER performance (Supplementary Fig. 12).

**Photothermal-assisted oxygen evolution reaction.** After PSAN-ligated NFO-12-7K NPs were identified as the most electrocatalytically active nanomaterials, we turned our attention to invoke photothermal effect of NFO-12-7K NPs in an attempt to reduce the activation energy $E_a$ of water splitting and promote the formation of electrocatalytically active oxyhydroxides (-OOH)\textsuperscript{[10]} for boosting OER reactivity. To this end, NFO-12-7K NPs were electrophoretically deposited on nickel foam (NF), which rendered intimate interfacial contact between NFO electrocatalysts and the underlying current collector (NF), thus decreasing the contact resistant and favoring electron and mass transport (Experimental Section and Supplementary Fig. 13-14). It is notable that in addition to the resulting PSAN-ligated NFO-12-7K/NF (hereafter referred to as NFO/NF) electrode prepared by electrophoresis as noted above, the bare nickel foam (denoted bare NF) was also selected as control sample for comparison.

First, UV-vis study was performed to examine the absorption characteristics of the samples. Clearly, compared to bare NF, the absorption edge of NFO/NF red-shifted and extended beyond 850 nm (Supplementary Fig. 15), suggesting that NFO/NF is capable of utilizing and converting more photons into heat under NIR irradiation. In this context, the spatial electric-field distribution and temperature distribution within NFO NP were theoretically modeled by the finite element method (FEM) (Fig. 4a). For a freestanding NFO NP ($d = 12$ nm), electric-field distribution at an excitation wavelength of 808 nm is shown in upper left panel of Fig. 4a. This light flux concentration and localized electromagnetic field enhancement would drive heat produced in NFO NP. The lower left panel of Fig. 4a illustrates the steady-state temperature distribution surrounding the NFO NP. Intriguingly, the close proximity of NFO NPs (with seven NFO NPs assembled together as an example) induces strong and respective coupling of electric-field distribution (central panel; Fig. 4a) as well as temperature distribution (right panel; Fig. 4a), clearly signifying that thermal energy is produced from photo-to-thermal conversion within NFO NPs.

To further elucidate photothermal responses of the electrodes, the temperature evolution of NFO/NF, bare NF electrodes, and 1.0 M KOH electrolyte under a NIR light irradiation (808 nm, 2.5 W cm$^{-2}$) was recorded by infrared imaging (Supplementary Fig. 16 and Fig. 4b). We note that direct irradiation of KOH electrolyte by NIR light showed an almost unchanged temperature (increase of less than 1 °C), which can be considered negligible for electrocatalysis. The temperatures of both NFO/NF and bare NF increased with the illumination time, reaching approximately 45 °C and 35 °C in 6 min, respectively. A 10 °C higher temperature than that of bare NF clearly suggests that NFO/NF is a potential photothermal electrode (Supplementary Fig. 16).
The stability of catalysts is a prerequisite for their long-term practical application. Prior to investigating the photothermal-assisted OER activity, the stability of NFO/NF was examined by a 12-h chronoamperometric test (Supplementary Fig. 17). The chronoamperometric curve shows the current density increased from ~16.56 to ~18.69 mA cm\(^{-2}\) (at 1.50 V vs. RHE), which can be attributed to an activation process taken place in the first 2 h.\(^{[20]}\) After that, it remained at ~18.69 mA cm\(^{-2}\) for 10 h, demonstrating an outstanding stability. The stability of this integrated electrode (i.e., NFO/NF) was further revealed by structural characterization of the used catalyst. SEM imaging on NFO/NF sample after electrochemical stability measurement showed no noticeable changes on the morphology of NFO/NF (Supplementary Fig. 18a-b), confirming that the NFO NPs were stable on the NF electrode even in alkaline OER conditions.

The photothermal-promoted electrocatalytic activity of NFO supported on NF electrode toward OER was then scrutinized using a photoelectrochemical cell containing an O\(_2\)-saturated 1.0 M KOH solution irradiated with 808-nm NIR light (Experimental Section; Supplementary Fig. 19). The circulating water was used to maintain the electrolyte at room temperature. As shown in Fig. 4c, the OER activity of NFO/NF was found to be progressively boosted, evidenced by higher current density \(j\) across all potentials and gradually decreased overpotential \(\eta_{20}\) from 307 mV (25 °C) to 272 mV (45 °C) at \(j = 20\) mA cm\(^{-2}\) (inset; Fig. 4c). The catalytic kinetic activities of NFO NPs were evaluated from the Tafel plots (Supplementary Fig. 20). The NFO/NF with the induction of photothermal effect by NIR irradiation (temperature raised to 45 °C) possessed prominently smaller Tafel slope for OER (43 mV dec\(^{-1}\)) than the same sample without experiencing NIR irradiation (67 mV dec\(^{-1}\); i.e., no photothermal effect and thus temperature remained at 25 °C), demonstrating highly favorable reaction kinetics toward oxygen evolution with the assistance of photothermal effect. Comparatively, under the same condition, the bare NF did not exhibit obvious NIR response (Supplementary Fig. 21a-b), where the overpotential and Tafel slope decreased from 434 mV (25 °C) to 416 mV (35 °C) (inset; Supplementary Fig. 21a) and from 143 mV dec\(^{-1}\) (25 °C) to 132 mV dec\(^{-1}\) (35 °C) (Supplementary Fig. 21b), respectively. As shown in Fig. 4d, the chronoamperometric \(J-T\) curves of bare NF and NFO/NF electrodes at a bias voltage in 1.0 M KOH electrolyte under NIR irradiation had similar sawtooth form and overall upward trend. For NFO/NF, upon each repeated on-off cycle, the current density manifested a rapid photoresponse with a depth of fluctuation of 2.5 mA cm\(^{-2}\). For comparison, the bare NF showed a negligible response to chopped NIR irradiation (a fluctuation of only 0.3 mA cm\(^{-2}\)). For NFO/NF, when the light was switched off, the current density promptly decreased yet higher than the initial value, which can be ascribed to the residual heat originated from the photo-to-thermal conversion. Clearly, these results verify that the NFO/NF electrode carries excellent photothermal conversion attribute for boosting OER performance. Remarkably, among an array of earth-abundant OER catalysts reported in literature (Supplementary Table 2), the NFO/NF crafted in this study emerges as one of highest-performance electrodes with the lowest overpotential (309 mV) at high current density of 100 mA cm\(^{-2}\) and very small Tafel slope (43 mV dec\(^{-1}\)) (Fig. 4e and Supplementary Table 2).
**Activation energy \( (E_a) \).** To further uncover the mechanism of photothermal effect on promoting the catalytic activity of NFO/NF during OER process, the activation energy \( E_a \) at the zero overpotential \( (\eta = 0) \) was calculated, which is widely regarded as an important descriptor for evaluating the performance of electrocatalysis.\(^{[21]} \) Derived from the LSV curves in Fig. 4c (for example, reading the current densities \( j \) at different temperatures for a given overpotential), the Arrhenius plots displayed the semilogarithmic dependences of \( j \) on the inverse temperature (see Experimental Section),\(^{[22]} \) that is, a linear relationship at varied overpotentials (Fig. 4f). Accordingly, \( E_a \) of NFO/NF at \( \eta = 0 \) was calculated to be 98.50 KJ mol\(^{-1} \) (Fig. 4g), much lower than 147.62 KJ mol\(^{-1} \) of bare NF (Supplementary Fig. 22b). This signifies that the photothermal heating induced by irradiating NFO NPs with NIR light can effectively lower the energy barrier for initiating OER and accelerate the sluggish OER reaction that undergo a four-electron transfer over a large thermodynamic potential (1.23 V). Meanwhile, the charge transfer resistance measurements (Supplementary Fig. 23-24) revealed the enhanced electron transport due to photothermal effect, which in turn led to improved OER reaction kinetics.

**Observation of dynamic active sites generation.** Earlier studies have revealed the importance of the oxidation of Ni\(^{2+} \) in Ni-based oxides for OER, where Ni\(^{2+} \) is susceptible to be oxidized to Ni\(^{3+} \) or a higher oxidation state. Such oxidation is believed to be a critical step in generating active oxyhydroxide sites, that is, \( \gamma \)-NiOOH, for OER.\(^{[23]} \) To study the dynamic oxidation of Ni\(^{2+} \) in NFO/NF electrode, the oxidation peaks between 1.32 V and 1.44 V in Fig. 4c were closely examined. The LSV curves of NFO/NF electrode exhibited an enhanced current density and a negatively shifted peak of Ni oxidation upon exposure to NIR light (Supplementary Fig. 25). This electrochemical behavior suggests that the surface of catalysts may undergo a dynamic reconstruction into oxyhydroxides, evolving into a more catalytically active surface for OER.\(^{[10]} \) Moreover, it is notable that the peak area ratio of Ni\(^{3+} / \)Ni\(^{2+} \) in Ni 2p increased from 0.58 (prior to photothermal-assisted OER reaction) to 1.06 (after photothermal-assisted OER reaction) (Supplementary Fig. 26a). And the peak area ratio of Fe\(^{3+} / \)Fe\(^{2+} \) in Fe 2p raised from 1.45 (before photothermal-promoted OER) to 1.69 (after photothermal-promoted OER) (Supplementary Fig. 26b). These ex-situ XPS results indicate that the increased high oxidation states of Ni and Fe were achieved via localized photothermal heating of NFO/NF during OER. Such surface reconstruction of NFO/NF electrode was also evidenced by ex-situ HRTEM where surface amorphous (Ni,Fe)oxyhydroxides were emerged (Supplementary Fig. 27).

**Scrutiny of photothermal-assisted electrocatalytic OER mechanism via operando Raman studies and DFT + U calculations.** To gain insight into the photothermal-promoted electrocatalytic activities, operando Raman spectra electrochemical measurements of NFO/NF electrodes in 1.0 M KOH were performed. Compared to the pristine states of both bare NFO powders and NFO/NF (i.e., without immersion in KOH) (Supplementary Fig. 28a), there was clear positive peaks shift of the NFO/NF electrode after being immersed in KOH under OCP (open circuit potential) condition, which is due to the decreased laser power attenuated the electrolyte.\(^{[24]} \) For bare NFO powders and NFO/NF, five peaks at 194, 313, 470, 541 and 679 cm\(^{-1} \) can be assigned to the corresponding Raman active bands of inverse spinel NiFe\(_2\)O\(_4\) (i.e., \( T_{2g(1)} \)),
E_g, T_{2g(2)}, T_{2g(3)}, and A_{1g}, respectively.\textsuperscript{[24]} In the case of NFO/NF electrode under OCP, the Raman peak at ~120 cm\textsuperscript{-1} can be ascribed to Ni(Fe) hydroxide species (Supplementary Fig. 28b),\textsuperscript{[25]} which was spontaneously formed after immersing the Ni(Fe)-based electrode into aqueous alkaline solution.\textsuperscript{[26]} Thus, the peak of T_{2g(1)} cannot be seen because of the partial overlapping.

It is important to note that the active modes between 400 and 700 cm\textsuperscript{-1} were potential dependent according to operando Raman measurements, indicating the electrode surface experienced a dynamic phase transformation in the potential range from OCP to 1.50 V, as clearly evidenced in Fig. 5a and Supplementary Fig. 29. As shown in Supplementary Fig. 29, for the NFO/NF electrode without being irradiated with NIR light (i.e., no photothermal effect), there were no shifts of the Raman peaks at 478, 563 and 692 cm\textsuperscript{-1} for potentials ≤ 1.39 V vs. RHE. It is noteworthy that as the potential increased to 1.41 V, the peaks at 474 and 554 cm\textsuperscript{-1} appeared, which are assigned to γ-NiOOH, suggesting the formation of Ni\textsuperscript{3+} species on the surface of electrode.\textsuperscript{[27]}

On the other hand, it is interesting to note that for the photothermal-promoted OER (Fig. 5a), the NFO/NF electrode displayed identical spectroscopic and electrochemical behavior when the potential was ≤ 1.35 V. Likewise, the γ-NiOOH phase emerged at 1.36 V, a 50 mV lower than the conversion potential of the electrode without experiencing photothermal heating (Supplementary Fig. 29). Moreover, much higher ratios of 474 cm\textsuperscript{-1} to 692 cm\textsuperscript{-1} (ΔI\textsubscript{2}) and 554 cm\textsuperscript{-1} to 692 cm\textsuperscript{-1} (ΔI\textsubscript{1}) were observed for NFO/NF with photothermal effect than those (ΔI\textsubscript{2} and ΔI\textsubscript{1}) without photothermal effect (Supplementary Fig. 30), suggesting the surface reconstruction into oxyhydroxide was more thorough for NFO/NF with photothermal effect. It is noteworthy that earlier reports of NiFe-based catalysts revealed that Fe ions would also be oxidized and reconstructed into oxyhydroxides.\textsuperscript{[28]} However, our operando Raman studies discussed above did not show the peaks of FeOOH species. This may be due to the relatively less amount of FeOOH produced during surface reconstruction, which is consistent with our ex-situ XPS results (Supplementary Fig. 26).

To further understand the effects of reconstructed oxyhydroxides on OER activity, first principles density functional theory plus Hubbard U (DFT + U) calculations based on the 4e-mechanism were employed to simulate the OER process on both the reconstructed (Ni,Fe)OOH and the original NFO structure models. As shown in Fig. 5b, (Ni,Fe)OOH model was consisted of 2D (Ni,Fe)O\textsubscript{2} layers intercalating with H\textsubscript{2}O molecules and K\textsuperscript{+} ions (see Supplementary Note 5), and the role of intercalated species were neglected during calculation because they have not been well characterized experimentally.\textsuperscript{[29, 30]} For inverse spinel NFO, half of the Fe\textsuperscript{3+} cations occupy the centers of tetrahedral sites, whereas Ni\textsuperscript{2+} and the remaining half of the Fe\textsuperscript{3+} occupy the octahedral sites (Supplementary Fig. 31 and Supplementary Note 5).\textsuperscript{[5]} The proposed 4e-mechanism of OER and the optimized structures of the intermediates in the free-energy landscape of (Ni,Fe)OOH and NFO are presented in Fig. 5c and Supplementary Fig. 32, respectively. The highest reaction free energy barriers on (Ni,Fe)OOH and NFO surfaces are 2.05 eV and 2.20 eV, respectively, implying the corresponding overpotentials η of 0.82 V and 0.97 V. The lower Gibbs free
energy on Ni atom sites of (Ni,Fe)OOH revealed a more favorable OER kinetics in reconstructed (Ni,Fe)OOH species. The calculation results highlight the pivotal role of (Ni,Fe)OOH species in improving catalytic reactivity.

It is worth noting that a suite of experiments discussed above demonstrated that the OER kinetics can be greatly facilitated by photothermal-enhanced surface reconstruction into highly active (Ni,Fe)OOH species, which in turn significantly improved intrinsic electrocatalytic activity. On the other hand, the formations of OH*, O* and OOH* display uphill energetics, signifying the reactions in (Ni,Fe)OOH system are endothermic at the applied voltage $U = 0$ V and $U = 1.23$ V (central panel; Fig. 5c). Taken together, the photo-to-thermal conversion would promote the oxygen evolution because of the assistance with localized heating.

Thus, a mechanism is proposed (Supplementary Fig. 33) to rationalize the observed reduction in activation energy (Fig. 4g), enhanced active Ni$^{3+}$ species generation (Fig. 5a), and subsequently improved OER activity (Fig. 4c) of the NFO/NF electrode under 808 nm NIR irradiation. The photothermal effect casts the following two profound impacts on the OER catalysis. First, upon NIR irradiation, thermal energy, arose from photo-to-thermal conversion of NFO NPs, could reduce the activation energy of water splitting, thus promoting kinetics of electrocatalytic reactivity (Supplementary Fig. 33a and Fig. 4g). Second, the judicious implementation of photothermal effect of NFO/NF electrode would also lower the energy barrier of Ni$^{2+}$ to Ni$^{3+}$ transformation (at a lowered potential (1.36 V) as opposed to 1.41 V without photothermal effect), and facilitate the surface reconstruction into more electrocatalytic active Ni$^{3+}$ oxyhydroxides species (Supplementary Fig. 33b, Fig. 5a and Fig. 5c), thereby boosting OER reactivity, as evidenced by LSV results in Fig. 4c. Moreover, given the semiconducting property of NFO NPs that can absorb and respond to NIR light (Supplementary Fig. 15), the holes generated by NIR irradiation on the NFO NP surface may render the oxidation of inactive Ni$^{2+}$ into active Ni$^{3+}$.

**Discussion**

In summary, we demonstrated the robustness of photothermal effect of inverse spinel oxides in promoting their surface reconstruction into oxyhydroxides (i.e., creating more dynamic active sites) for markedly enhanced OER catalysis, as unraveled by operando Raman spectra-electrochemistry study. First, spinel oxide NFO NPs of tunable sizes that are permanently ligated by polymers of different lengths (i.e., PSAN-ligated NFO NPs) are synthesized by capitalizing on amphiphilic star-like PAA-b-PSAN diblock copolymers as nanoreactors. Subsequently, investigation into the effects of the NP size and surface PSAN chain length reveals that NFO NPs of the largest size ligated with shortest PSAN chains manifest outstanding OER reactivity due to the presence of the highest fraction of accessible electrochemically-active surface area and the fastest reaction rate. Afterwards, photothermal effect is introduced to the NFO/NF electrode via NIR light, yielding a considerably reduced overpotential from 307 mV (25 °C; in the absence of photothermal heating) to 272 mV (45 °C; after photothermal heating) at 20 mA cm$^{-2}$ and a
small Tafel slope of 43 mV dec\(^{-1}\). Such localized photothermal heating effectively lowers the charge transfer resistance and the activation energy for OER.

Most importantly, the structures of active phase and the reaction mechanism are uncovered by combining \textit{operando} Raman spectra electrochemical measurements and DFT + U calculations. Under applied anodic potentials, the surface of NFO NPs are found to transform into active (Ni,Fe)oxyhydroxides species. In contrast to applied potential of 1.41 V for non-photothermal-assisted OER, the surface of NFO NPs dynamically reconstructed into active γ-NiOOH phase occurs at lower applied potential of 1.36 V under OER condition with photothermal effect, as unveiled by \textit{operando} Raman study, and the high OER activity of (Ni,Fe)OOH species is also supported by DFT calculations. Our study brings fundamental and practical insights into the effectiveness of \textit{in-situ} heating enabled by photo-to-thermal conversion of photothermal nanomaterials in promoting electrocatalysis. Compared to expensive plasmonic nanomaterials such as Au and Ag NPs, the use of earth-abundant transition metal-based materials (oxides, sulfides, phosphides, etc.) capable of photothermal conversion may open up new avenues for more efficient catalytic water splitting and related energy conversion systems.

\section*{Methods}

\textbf{Synthesis of PSAN-ligated NiFe\(_2\)O\(_4\) Nanoparticles (PSAN-ligated NFO NPs).} By capitalizing on star-like PAA-\textit{b}-PSAN diblock copolymers as nanoreactors, PSAN-ligated NFO NPs were synthesized. In a typical procedure, star-like PAA-\textit{b}-PSAN (10 mg) was dissolved in 0.2 mL DMF at room temperature, followed by the addition of 9 mL DPE. An appropriate amount of precursors (Ni(OAc)\(_2\) and Fe(AcAc)\(_3\)) were added, where the molar ratio of acrylic acid (AA) units in PAA blocks to precursors was set at 1:10 in order to maximize the loading of precursors into the compartment containing PAA blocks. The mixture was stirred under \(\text{N}_2\) at 80 °C for 12 h to ensure that all precursors were well dissolved in DMF and the PAA blocks-containing compartment was fully loaded by precursors. Subsequently, 1 mL BA was added into the reaction system to swell the inner PAA chains as it is a good solvent for PAA yet poor solvent for PSAN. The reaction was then carried out at 250 °C. After reaction for 4 h, the resulting PSAN-ligated NFO NPs were collected by centrifugation and washed with ethanol several times to remove unreacted precursors and mixed solvent. For comparison, NFO NPs templated by star-like PAA homopolymers as well as NFO NPs without the use of any templates were also synthesized by a similar procedure and used as control samples. Further details are available in the \textit{Supplementary Experimental Section}.

\textbf{Characterization.} Number-average molecular weight (M\(_n\)) and polydispersity index (PDI) of star-like polymers were measured by gel permeation chromatography (GPC) equipped with an LC-20AD HPLC pump and a refractive index detector (RID-10A, 120 V) at 35 °C. A series of monodisperse polystyrene in THF were used as standard to calibrate the GPC at a flow rate of 1.0 mL min\(^{-1}\). \(^1\)HNMR spectra of star-like PtBA and star-like PtBA-\textit{b}-PSAN used CDCl\(_3\) as solvent and were recorded using a Varian VXR-300 spectroscope. Dynamic light scattering (DLS) data was acquired using laser light scattering spectrometer (Malvern Autosizer 4700) at 25 °C. The size of PSAN-ligated NFO NPs were examined by TEM (JEOL 100;
operated at 100 kV) and high-resolution TEM (TECNAIG2 F30; operated at 300 kV). The crystalline structures of PSAN-ligated NFO NPs were evaluated by XRD (X’pert PRO, The Netherlands). X-ray photoelectron spectroscopy (XPS) was measured by the Thermo Scientific K-Alpha XPS system. The UV-vis absorption spectra of NFO/NF and bare NF were measured by Shimadzu UV-vis-2450 spectrometer. Raman spectra for bare NFO powders and NFO/NF samples were collected using a Renishaw inVia Raman microscope with an excitation wavelength of 532 nm, a power of 10 mW, and an acquisition time of 10 s.

**Electrochemical Measurements.** The OER activities of catalysts were measured in a three-electrode glass cell filled in 1.0 M KOH electrolyte on a Zennium PP211 electrochemical workstation using an Ag/AgCl electrode as the reference electrode, a carbon rod as the counter electrode, and the glassy carbon (GC, area, 0.19625 cm$^2$) loaded with catalysts as the working electrode. The catalyst ink was prepared by dispersing 1 mL of the 5 mg mL$^{-1}$ PSAN-ligated NFO NPs in DMF, 2 mg of carbon black and 80 µL Nafion solution (5 wt%) by sonication for 40 min to form a homogenous ink. Next, 20 µL of the ink was loaded onto GC working electrode. The ink was dried slowly in air until a uniform catalyst covered on the working electrode surface was formed. The detailed protocol is provided in *Supplementary Experimental Section.*

**Photothermal-promoted Electrocatalytic OER Measurements.** To investigate the photothermal-promoted OER performance, PSAN-ligated NFO NPs was electrophoretically deposited onto nickel foam (NF; area = 1.0 cm$^2$), which was used as the working electrode. As shown in *Supplementary Fig. 13*, for electrophoretic deposition of PSAN-ligated NFO NPs from their DMF solution onto NF substrates, 5 mg mL$^{-1}$ of 5 mL PSAN-ligated NFO NPs DMF solution was transferred into a vial, and two pieces of NFs (1.0 cm × 5.0 cm) serving as substrates were inserted in parallel with a fixed gap of ~8 mm and then connected to a DC power supply. With increasing time, the NPs in DMF solution moved toward the NF and were assembled onto the NF. Then, the as-prepared PSAN-ligated NFO NPs deposited on NF (denoted NFO/NF) were dried at 80 °C for 2 h. The mass loading of NFO NPs (≈0.2 mg cm$^{-2}$) was determined by weighing the NF substrate before and after electrophoresis. The photothermal-promoted electrocatalytic tests were conducted using a photoelectrochemical cell containing an O$_2$-saturated 1.0 M KOH solution irradiated with an 808 nm NIR light (irradiation power = 2.5 W cm$^{-2}$) (*Supplementary Fig. 19*). The circulating water was used to make sure the temperature of electrolyte remain at room temperature. The temperature of the working electrode was monitored by an IR thermal camera (FLIR One Pro) for every 2 s until the electrode reached a steady temperature. Chronoamperometry was carried out at a fixed potential to test the stability of catalyst.

The activation energy ($E_a$) for NFO/NF and bare NF were calculated from the slope of the modified Arrhenius plot:

$$j = Ae^{(-E_a/RT)}$$

where $j$ is current density, $A$ is pre-exponential factor, $E_a$ is activation energy, $R$ is gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is Kelvin temperature.
**Operando Raman Measurements.** Operando Raman spectra were collected under a controlled constant potential applied from open circuit potential (OCP) to 1.50 V vs. RHE. A Teflon electrochemical cell with a quartz window was used, consisting of a working electrode (NFO/NF) at the top, a Pt wire counter electrode and an Ag/AgCl (saturated KCl) reference electrode. Raman spectra were acquired using a microscope (inVia Raman microscope, Renishaw) with an excitation wavelength of 532 nm, a power of 10 mW, and an acquisition time of 10 s. Spectral shifts were calibrated routinely against the value of a silicon wafer (520.7 cm\(^{-1}\)).

**FEM Simulation.** The finite-element method (FEM) (COMSOL software) was used to study the electromagnetic field distribution and temperature distribution. Typically, a NFO NP absorbs NIR light (wavelength = 808 nm, and irradiation power = 2.5 W cm\(^{-2}\)), triggering the increase of localized electromagnetic field, concentrating light energy on the NP, and delivering light-to-heat transformation as heat is generated. The optical absorption and generated volume power intensity could be calculated by FEM Solutions, and was subsequently used as heat input for the temperature simulation. The basic heat transfer equation is given below:

\[
\frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + \rho C_p \frac{T^* - T}{\tau} + q_{\text{in}}
\]

where \(x\) and \(t\) are the space vector and time, respectively. Thermal conductivity \((k)\), density \((\rho)\) and heat capacity \((C_p)\) of NP were taken from the literature.\[^{31}\] is the local temperature, and \(T^*\) represents the thermal energy induced by photo-to-thermal conversion within NFO NPs.

**First-principles Calculation.** All the free energies were calculated using the generalized gradient approximation (GCA) and the Perdew-Burke-Ernzerhof functional for the exchange correlation to the density functional theory (DFT). The projected augmented wave method was used, as implemented in Cambridge serial total energy package (CASTEP) code.\[^{32}\] It is well known that the localized nature of 3d electrons is difficult to be accurately described by GCA, thus the effective on-site Hubbard \(U_{\text{eff}}\) correction on the 3d or 4d electrons for all the transition metals included in our calculation were also employed.\[^{33}\] The \(U_{\text{eff}}\) parameter was taken from the previous theoretical reports, that is, 4.2 eV and 6.4 eV for Fe and Ni, respectively.\[^{34,35}\] A 3D slab model with periodic boundary conditions was used with an energy cutoff of 500 eV and an appropriate \(\gamma\)-point, \(3 \times 3 \times 1\) mes, was selected to ensure that the total energies converged within 5 meV per formula unit.

The OER based in an alkaline electrolyte undergoes the following four elementary steps:

\[
* + \text{OH}^- \rightarrow \text{OH}* + e^- \quad (1)
\]

\[
\text{OH}* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + e^- \quad (2)
\]

\[
\text{O}^* + \text{OH}^- \rightarrow \text{OOH}* + e^- \quad (3)
\]

\[
\text{OOH}* + \text{OH}^- \rightarrow * + \text{O}_2 + \text{H}_2\text{O} + e^- \quad (4)
\]

where \(^*\) represents an active site on the catalyst surface; \(\text{OH}^*, \text{O}^*, \text{and OOH}^*\) are the oxygen intermediates.
The computational hydrogen electrode model proposed by Norskov and co-workers was used to express
the thermochemistry of the sub-reactions at any given pH and applied potential U. The Gibbs free
ergies were calculated from total energies as:
\[ \Delta G_i = \Delta E_i + \Delta ZPE_i - T \Delta S_i \]  
where \( i = 1, 2, 3, 4 \) corresponds to steps from Eq. (1) to Eq. (4).

The Gibbs free energy changes for each step were calculated using the following equations:
\[ \Delta G_1 = G(OH^*) - G(*) - \mu_{OH} \]
\[ = E(OH^*) - E(*) - \frac{1}{2}E(H_2O) + 1/2E(H_2) - eU + \Delta \text{(pH)} + \Delta(ZPE - T \Delta S) \]  
\[ \Delta G_2 = G(O^*) + \mu_H - G(OH^*) \]
\[ = E(O^*) + 1/2E(H_2) - E(OH^*) - eU + \Delta \text{(pH)} + \Delta(ZPE - T \Delta S) \]  
\[ \Delta G_3 = G(OOH^*) - G(O^*) - \mu_{OH} \]
\[ = E(OOH^*) - E(O^*) - E(H_2O) + 1/2E(H_2) - eU + \Delta \text{(pH)} + \Delta(ZPE - T \Delta S) \]  
\[ \Delta G_4 = 4 \times [1.23 \text{ eV} - eU + \Delta \text{(pH)}] - (\Delta G_1 + \Delta G_2 + \Delta G_3) \]  
\[ \]  
where the zero point energy (ZPE) and entropy correction values (TS) are listed in the Supplementary Table 3 and 4. \( eU \) represents the free energy changes for one electron transfer, where \( U \) is electrode potential with respect to the standard hydrogen electrode. For \( pH \neq 0 \), \( \Delta \text{(pH)} \) should be defined as \( -k_B T \log(pH) \), \( k_B \) is Boltzman constant \( (1.380649 \times 10^{-23} \text{ J/K})[36] \), and \( k_B T \) is 0.025692 eV \((T = 298.15 \text{ K})\).

The theoretical overpotential \( \eta^{\text{OER}} \), which is independent of pH, was then given by Eq. (10):
\[ \]  
\[ \]  
**Data availability.** The data that support the findings of this study are available from the corresponding author upon request.

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Declarations

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Author Contributions

Z.L., L.G. and X.C. conceived and designed the experiments. L.G., X.C. conducted the experiments and contributed equally to this work. Z.W., C.S., Z.L., S.L., M.Z., J.L. performed characterizations. Y.H provided DFT calculations. L.G., X.C. and Z.L. collectively wrote the paper. All authors commented on the final manuscript.

Additional information

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Competing Interests

The authors declare no competing interests.

Figures
Figure 1

Stepwise representation of the synthesis of hairy PSAN-ligated spinel oxide NiFe2O4 nanoparticle (NFO NP). Amphiphilic star-like PAA-b-PSAN diblock copolymer is employed as nanoreactor to template the growth PSAN-ligated NFO NP. Star-like PAA-b-PSAN is synthesized by sequential ATRP of tBA monomers and St and AN co-monomers using 21Br-β-CD as macroinitiator (i.e., forming star-like PtBA-b-PSAN), followed by hydrolysis of inner hydrophobic PtBA blocks into hydrophilic PAA blocks.
Figure 2
TEM images of PSAN-ligated NFO NPs synthesized using amphiphilic star-like PAA-b-PSAN diblock copolymers as nanoreactors. (a-d) TEM images of NFO-3-8K, NFO-7-15K, NFO-12-21K and NFO-12-7K (Table S1). (e) TEM image of NFO-12-7K after staining with RuO4, where the PSAN blocks are preferentially stained by RuO4 and appeared relatively lighter situated on the surface of dark NFO NP.
core. Scale bar in inset is 20 nm. The yellow circles are the guides to eyes. (f) HRTEM image of NFO-12-7K.

**Figure 3**

Comparison of OER activities of as-prepared PSAN-ligated NFO NPs electrocatalysts. (a) LSV curves, (b) the double-layer capacitance (Cdl) plots, (c) corresponding Tafel plots, (d) histograms of NFO-3-8K, NFO-7-15K, NFO-12-21K and NFO-12-7K electrocatalysts for OER in 1.0 M KOH, from which the overpotentials, onset potentials, Tafel slopes and Cdl values can be obtained and compared. All measurements were performed on glassy carbon (GC) electrodes in O2-saturated 1.0 M KOH at 5 mV s⁻¹ and 1600 rpm. The iR drop from the solution resistance was compensated at 95%.
Figure 4

Photothermal ability of NFO NPs and photothermal-assisted OER activities of NFO/NF electrodes. (a) Spatial electric field distribution (upper left panel) and temperature distribution (lower left panel) for an NFO NP (d = 12 nm), as well as 3D electric field distribution (central panel) and temperature distribution (right panel) in x-y-z direction for seven NFO NPs (d = 12 nm), by FEM modeling (a COMSOL software). (b) Infrared images of NFO/NF under NIR irradiation. (c) Photothermal electrochemical activities toward OER for NFO/NF electrode measured at different electrode temperatures induced by NIR light. Inset shows the decrease of overpotential at j = 20 mA cm\(^{-2}\) with the increase of temperature. (d) Chronoamperometric J–T curves of bare NF and NFO/NF electrodes at a bias voltage under chopped illumination for OER. (e) Comparisons of overpotentials at 100 mA cm\(^{-2}\) and Tafel slopes of reported earth-abundant OER electrocatalysts. (f) Arrhenius plots for the NFO/NF electrode, showing
semilogarithmic dependence of current densities $j$ on inverse temperatures $T$ at various overpotentials $\eta$. Five $\eta$ are taken from 240 mV to 320 mV at an interval of 20 mV. (g) Activation energy $E_a$ at the zero overpotential ($\eta = 0$) obtained through extrapolation to $\eta = 0$.

Figure 5

An integrated operando Raman spectra-electrochemistry and DFT + U calculation study for unravelling the photothermal effect on promoting the generation of reconstructed (Ni,Fe)oxyhydroxides on the NFO surface. (a) Operando Raman spectra of NFO/NF with photothermal effect (i.e., irradiated with 808-nm NIR light) from open circuit potential (OCP) to 1.50 V vs. RHE in 1.0 M KOH. (b) The model crystal structure with chemical formula of $K_{1/3}(H_2O)_{2/3}(Ni, Fe)O_2$ for the reconstructed surface, that is, (Ni,Fe)OOH (color-coded balls are as follows: green - Ni; dark gray - Fe; purple - K$^+$; red - O; white - H). (c) Schematic of the Gibbs free energy changes on (Ni,Fe)OOH and NiFe2O4 at different applied potential $U$ for the four elementary steps during the OER based on DFT + U calculations (central panel). The proposed 4e-mechanism and optimized intermediates structures of (Ni,Fe)OOH are shown in the periphery. The Ni ion (*Ni) in (Ni,Fe)OOH is active site.

Supplementary Files

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