Nitrogen-incorporation activates NiFeOₓ catalysts for efficiently boosting oxygen evolution activity and stability of BiVO₄ photoanodes

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Developing low-cost and highly efficient catalysts toward the efficient oxygen evolution reaction (OER) is highly desirable for photoelectrochemical (PEC) water splitting. Herein, we demonstrated that N-incorporation could efficiently activate NiFeOₓ catalysts for significantly enhancing the oxygen evolution activity and stability of BiVO₄ photoanodes, and the photocurrent density has been achieved up to 6.4 mA cm⁻² at 1.23 V (vs. reversible hydrogen electrode (RHE), AM 1.5 G). Systematic studies indicate that the partial substitution of O sites in NiFeOₓ catalysts by low electronegative N atoms enriched the electron densities in both Fe and Ni sites. The electron-enriched Ni sites conversely donated electrons to V sites of BiVO₄ for restraining V⁵⁺ dissolution and improving the PEC stability, while the enhanced hole-attracting ability of Fe sites significantly promotes the oxygen-evolution activity. This work provides a promising strategy for optimizing OER catalysts to construct highly efficient and stable PEC water splitting devices.
**Photoelectrochemical (PEC) water splitting has been considered as a promising strategy for converting solar light into hydrogen energy.** To achieve its practical applications, the design and fabrication of semiconductor photoanodes with sufficient light absorption, effective charge separation, and high surface reactivity are essentially required. Among various candidates, bismuth vanadate (BiVO₄) has been attracting particular attentions owing to its appropriate bandgap (2.4 eV) and suitable band-edge positions. However, suffering from the high charge-recombination and sluggish oxygen evolution reaction (OER) kinetics, most of reported photocurrent densities of BiVO₄ photoanodes are far below the theoretical expectation (7.5 mA cm⁻², AM 1.5 G illumination, 100 mW cm⁻²). During past decades, diverse strategies have been developed to improve the PEC activities of BiVO₄ photoanodes, including elemental doping, facet tailoring, and heterojunction, etc. Although the PEC performances have been increased to a certain extent owing to the improved carrier mobility as well as electrical conductivity, the intrinsically poor surface reactivity still seriously restricts the PEC conversion efficiency. Recently, BiVO₄ photoanodes decorated with various transition-metal catalysts have been extensively reported for remarkably promoting the OER activities. Specifically, they could efficiently extract photo-generated holes, minimize over potential, and provide active sites, which are all beneficial to accelerate the PEC water oxidation kinetics. Among various OER catalysts, the VIII metal (Fe, Co, Ni) oxides or (oxy)hydroxides, especially for NiFe-based materials, have attracted particular interests in recent years. For example, Domen et al. deposited NiFe bimetallic catalyst on BiVO₄ photoanodes for improving the PEC activities up to 4.2 mA cm⁻² at 1.23 V RHE. Zhang and co-workers reported that BiVO₄ photoanodes modified with NiFe complexes exhibited an excellent photocurrent of 5.10 mA cm⁻². Pihosh et al. fabricated a WO₃/BiVO₄/CoPi core-shell nanostructured photoanode that achieves near 90% of the theoretical water splitting photocurrent. On this basis, Kosar et al. acquired a highly efficient solar-to-hydrogen conversion efficiency of 7.7% by photovoltaic cell and WO₃/BiVO₄/CoPi core-shell nanorods PEC cell tandem. Despite the crucial roles of OER catalysts for enhancing PEC behaviors have been well established, much less attentions focused on optimizing their electronic structures to further boost the PEC conversion efficiency, especially for bimetallic catalysts.

Herein, we reported the incorporation of non-metallic nitrogen-atom into NiFeOₓ catalysts to rationally tailor the electronic structure, which remarkably promoted the photocurrent density of BiVO₄ photoanodes up to 6.4 mA cm⁻² at 1.23 V RHE under AM 1.5 G (100 mW cm⁻²) with an excellent durability. The outstanding PEC performances should be attributed to the electronic reconstruction in both NiFeOₓ and BiVO₄, resulting from the partial substitution of O sites by low electronegativity N atoms. Specifically, the weak electron-attracting capacity of N atoms led to the electron enrichments on both Fe and Ni sites. Subsequently, the electron injection from Ni atoms to lattice V sites of BiVO₄ was favorable for improving the oxygen-evolution stability, while the Fe sites could effectively attract holes for promoting the PEC activity. This work firstly demonstrates the rational regulation of electronic structures in OER catalysts as well as fundamental understanding of their intrinsic roles in PEC oxygen evolution reaction.

**Results**

**Morphology and structure characterizations.** The nanoporous BiVO₄ photoanodes supported on F-doped SnO₂ (FTO) glass substrates were fabricated by an electrochemical deposition associated with calcination treatment. Figure 1a shows the scanning electron microscopy (SEM) images of the obtained BiVO₄ photoanodes, clearly revealing their unique worm-like porous structure with an average diameter of 200–300 nm. Additionally, the high-resolution transmission electron microscopy (HR-TEM) image (Supplementary Fig. 1) clearly indicates that these nanocrystals possess a relatively smooth surface and a lattice spacing of 0.311 nm corresponded to (−130) plane of monoclinic BiVO₄ phase. Interestingly, after the decoration of...
N:NiFeOx catalysts, the smooth surfaces of pristine BiVO4 photoanodes transformed into a rough flocculent-structure (Fig. 1b). The HR-TEM images (Fig. 1c and Supplementary Fig. 2) clearly indicate that an amorphous layer of N:NiFeOx catalysts was uniformly covered on BiVO4 surfaces with a thickness of ~4 nm. Moreover, Fig. 1d and Supplementary Fig. 3 show the energy dispersive spectroscopy (EDS) elemental line and mapping images, revealing the uniform distributions of N, Ni and Fe elements on BiVO4 crystal surfaces. Besides, the X-ray photoelectron spectroscopy (XPS) result also confirms the successful incorporation of the nitrogen element into the NiFeOx layer (Supplementary Fig. 4). However, compared with pristine BiVO4 photoanodes, no evident peak change could be observed in the X-ray diffraction (XRD) patterns after the decoration of N:NiFeOx catalysts (Supplementary Fig. 5), which should be due to their amorphous structure and ultrathin thickness.

**Photoelectrochemical properties.** The PEC water splitting performances of N:NiFeOx catalyst decorated BiVO4 photoanodes (marked as BiVO4/N:NiFeOx) were measured in 0.5 M K$_2$BO$_3$ (pH ≈ 9.5) electrolyte under AM 1.5 G illumination (100 mW cm$^{-2}$). For comparison, the PEC activities of pristine BiVO4 as well as NiFeOx decorated BiVO4 photoanodes (marked as BiVO4/NiFeOx) have also been studied. As shown in Fig. 2a and Supplementary Fig. 6, the pristine BiVO4 photoanodes exhibit a relatively low photocurrent density (2.1 mA cm$^{-2}$ at 1.23 V RHE), suffering from the sluggish oxygen evolution kinetics at anode/electrolyte interfaces. Obviously, the decoration of NiFeOx catalysts on BiVO4 photoanodes could significantly promote the photocurrent density to an extent due to the electron-hole separation, and the increased interface charge transfer and ultrathin thickness of N:NiFeOx catalysts (Supplementary Fig. 8). Figure 2c shows the decay-time (t-t) fitting results (Supplementary Table 2), the calculated HC-ABPE values of BiVO4/N:NiFeOx photoanodes could be achieved to 93%, which is much higher than BiVO4 (8%) and BiVO4/NiFeOx (54%). The above results clearly reveal that the incorporation of N atoms in NiFeOx catalysts not only significantly promotes the oxygen evolution activity but also effectively enhances the PEC stability of BiVO4 photoanodes.

Furthermore, their incident photon to current conversion efficiencies (IPCEs) were conducted and shown in Fig. 2d (Supplementary Fig. 14). At the wavelength of 360 nm, the IPCE values of BiVO4/N:NiFeOx photoanodes could be achieved to 93%, which is much higher than BiVO4 (8%) and BiVO4/NiFeOx (54%). Figure 2e shows the electrochemical impedance spectroscopy (EIS) for further elucidating the interfacial charge transfer and oxygen evolution kinetic. According to the Nyquist plots and the fitting results (Supplementary Table 2), the calculated resistance values of BiVO4/N:NiFeOx, BiVO4/NiFeOx, and BiVO4 photoanodes were 139.5, 149.8, and 458.9 Ω, respectively, revealing the preferable capability of N:NiFeOx catalyst for facilitating interface charge transfer. Moreover, the hydrogen and oxygen evolution kinetics at anode/electrolyte interfaces. Obviously, the decoration of NiFeOx catalysts on BiVO4 photoanodes could improve the PEC stability to a certain extent, the photocurrent density also decreased down to 2.8 mA cm$^{-2}$ after 5 h test. Interestingly, BiVO4/N:NiFeOx photoanodes possess the excellent photocurrent stability during the whole test process, indicating the positive effects of N:NiFeOx on restraining V$^{2+}$ dissolution from BiVO4 lattices and the obtained photoanodes with excellent structural stability (Supplementary Fig. 11, Figs. 12 and 13, and Table 1).

![Fig. 2 Photoelectrochemical properties.](https://example.com/fig2)

**Fig. 2 Photoelectrochemical properties.** a Linear-sweep voltammograms (LSV, with a scan rate of 10 mV s$^{-1}$), b half-cell ABPE (HC-ABPE) results, c I-t stability tests measured at 1.23 V vs. RHE, d IPCE results at 0.6 V vs. RHE and e EIS results at 0.75 V vs. RHE under illumination for BiVO4, BiVO4/NiFeOx, and BiVO4/N:NiFeOx photoanodes, f H$_2$ and O$_2$ evolution of BiVO4/N:NiFeOx measured at 1.23 V vs. RHE. All the measurements were carried at 0.5 M K$_2$BO$_3$ (pH = 9.5) electrolyte.
The photoluminescence spectroscopy (PL) has been measured by a fluoroscence spectrophotometer under laser excitation of 355 nm. As shown in Fig. 3a, two PL peaks can be clearly identified. More specifically, the peak at 470 nm is associated with FTO (SnO₂) substrate (Supplementary Fig. 15). The peak at 493 nm near the absorption band edge of BiVO₄ (Supplementary Fig. 16) is attributed to radiative recombination of hole in O 2p band and electron in V 3d band, which represents the charge recombination ability [41, 42]. Specifically, the pristine BiVO₄ photoanodes exhibited a very strong PL peak, demonstrating the relatively high electron-hole recombination ratios. However, after the decoration of OER catalysts, the PL peak intensities have been evidently reduced. More specifically, N:NiFeOₓ catalysts exhibit more efficient separation and extending the carriers lifetimes. Figure 3d shows their interfacial charge transfer (ηtrans) efficiencies for water oxidation reaction (Supplementary Fig. 18). The pristine BiVO₄ exhibits a very low efficiency of 28% at 1.23 V_RHE, while the surface deposition of NiFeOₓ and N:NiFeOₓ catalysts could effectively increase the ηtrans efficiencies up to 66.3 and 88%, respectively. Furthermore, their electrochemical OER properties under dark conditions have also been studied and shown in Fig. 3e. Obviously, BiVO₄/N:NiFeOₓ possesses a lower over-potential and higher water oxidation current compared with BiVO₄ and BiVO₄/NiFeOₓ, further revealing its excellent OER activity. The large-scale fabrication of photoanodes should be necessarily required for future practical applications. Accordingly, the dual BiVO₄/N:NiFeOₓ photoanodes with a relatively large area (2 × 3.5 cm²) have been fabricated, and the photocurrent could achieve up to 37 mA at 1.23 V_RHE accompanied with an excellent stability of 10 h (Fig. 3f). Thus, the above results clearly demonstrate that the BiVO₄/N:NiFeOₓ photoanodes possess the tremendous potential for practical PEC water splitting applications.

**Effects of N-incorporation into BiVO₄/NiFeOₓ films.** Furthermore, the effects of the N-incorporation on the surface chemical states and electronic structures of both NiFeOₓ and BiVO₄ have been explored by XPS. As shown in Supplementary Figs. 19 and 20, no evident change could be detected in Bi 4f peaks of BiVO₄/NiFeOₓ compared with BiVO₄/NiFeOₓ and BiVO₄, revealing the negligible influence of N-substitution on the Bi sites of BiVO₄ photoanodes. Interestingly, compared with BiVO₄/NiFeOₓ samples, a shoulder peak at lower binding energy positions could be observed in V 2p spectra of BiVO₄/N:NiFeOₓ photoanodes (Fig. 4a), which should be attributed to the formation of V^{(5–x)+} species. Moreover, the relative ratio of Ni^{2+} species in BiVO₄/N:NiFeOₓ has been evidently increased (Fig. 4b) [46–50], while the Fe^{3+} ratio has been decreased compared with BiVO₄/NiFeOₓ samples (Fig. 4c) [51–53]. On the basis of
above results, it may be proposed that the partial substitution of O sites in NiFeOx catalysts by N atoms should enrich the electron densities in Fe and Ni sites. Furthermore, the electron-enriched Ni sites conversely donated electrons to V sites of BiVO4 for restraining V$^{5+}$ dissolution and improving the PEC stability. Additionally, the electron-enriched Fe sites could efficiently attract photo-generated holes from BiVO4 surfaces, which significantly promoted the oxygen-evolution activity. Thereby, the N-incorporation in NiFeOx catalysts could effectively promote the oxygen evolution activity and stability of BiVO4 photoanodes. To further confirm the above speculations, the N atoms in N:NiFeOx catalysts were replaced by O atoms again via an oxygen plasma treatment. As shown in Supplementary Figs. 20 and 21, all the XPS peaks of Fe, Ni, Bi, and V elements were nearly consistent with BiVO4/NiFeOx photoanodes. Additionally, after the replacement of N with O atoms, the photocurrent density has been obviously reduced from 6.4 to 5 mA cm$^{-2}$ at 1.23 V_RHE accompanied by the poor PEC water oxidation stability (Supplementary Fig. 22), confirming the crucial roles of N-incorporation in promoting the OER activity and PEC stability of BiVO4 photoanodes.

DFT calculation and analysis. Furthermore, the density functional theory (DFT) calculation has been performed to reveal the change of electron densities in Fe and Ni sites after incorporation of N atoms. As shown in Fig. 4d, e, the charge density difference results clearly reveal that the electron densities at Fe and Ni sites increased significantly (yellow regions) after partial substitution of O sites with N atoms in NiFeOx catalysts. Additionally, the Bader charge analysis (Supplementary Table 4) also verified the enriched electron densities in N: NiFeOx catalysts. Consequently, the N-incorporation, which is highly consistent with the XPS results. Thereby, these calculation results could further provide supports on the crucial roles of N-incorporation in regulating the electronic structures of NiFeOx.

Discussion

In summary, we reported a facile N-incorporation method to rationally regulate the electronic structures of NiFeOx catalyst decorated on BiVO4 photoanodes. More detailed experiments and XPS analysis reveal that owing to the relatively low electronegativity of N atoms, their incorporation in NiFeOx catalysts facilitates the electron enrichments in Fe and Ni sites. Furthermore, the Ni sites would donate electrons to V sites on BiVO4 surface, which could efficiently restrain V$^{5+}$ dissolution and improve the PEC water oxidation stability. Moreover, the enhanced hole-attracting ability of Fe sites significantly promotes the oxygen-evolution activity. As expected, the BiVO4/N: NiFeOx photoanodes exhibited an outstanding photocurrent density of 6.4 mA cm$^{-2}$ at 1.23 V_RHE (AM 1.5 G, 100 mW cm$^{-2}$) accompanying with the enhanced PEC stability. This work provides a new insight to construct highly efficient and stable OER catalysts for fabricating high-efficiency PEC devices.

Methods

Materials. All chemicals were of analytical grade purity, obtained from Sinopharm Chemical Reagent Co., Ltd., and used as received without further purification.

Synthesis of nanoporous BiVO4 photoanodes. The nanoporous BiVO4 photoanode was obtained based on the previous report$^{10}$. 2 mM Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 0.4 M KI solution (50 mL). Then, the pH value of this solution was adjusted to 1.7 by HNO$_3$. Subsequently, 0.23 M quinhydrone was dispersed into ethanol solution (20 mL). Finally, mixing the two solution and stirring vigorously for a few minutes to acquire the electrodeposited solution. The cathodic deposition was performed at a constant potential of −0.1 V vs. Ag/AgCl for 3 min at room temperature to obtain the BiOI electrodes, among which FTO, Ag/AgCl (4 M KCl), and platinum pair were used as working electrode (WE), reference electrode (RE) and counter electrode (CE), respectively. Then, VO(acac)$_2$ (0.2 M, 0.2 mL) dissolved in DMSO (10 mL) solution was coated on the BiOI electrodes and heated in the air at a muffle furnace at 450 °C for 2 h (cycling rate = 2 °C/min) to convert to BiVO4. After calcination, the excess V$_2$O$_5$ on the electrode surface was soaked into deionized water and calcined at 300 °C for 1 h in a muffle furnace in air atmosphere to obtain the BiVO$_4$/NiFeO$_x$ samples. The synthesis of BiVO4/NiFeOx and BiVO4/O$_2$-NiFeO$_x$ photoanodes was the same as the above steps for the preparation of BiVO4/NiFeO$_x$, except that the final calcination process is changed to a N$_2$ or O$_2$ plasma treatment for 5 min (a medium power of 10.5 W and a pressure of
Synthesis of BiVO₄/NiFeP and BiVO₄/NiFeOx photoanodes. The BiVO₄ photoanodes were immersed into the fresh metal salt solution (2.5 mL of 10 mM FeCl₃·6H₂O and 7.5 mL of 10 mM NiCl₂·6H₂O), and then a NaBH₄ aqueous solution was added dropwise. The solution was stood for 50 min. Finally, the electrodes were washed by deionized water to obtain the BiVO₄/NiFeP photoanodes. Firstly, the BiVO₄ films were dipped into a water solution (20 mL) containing SnCl₂ (0.8 g) and HCl (40 wt%, 0.8 mL) for 2 min. Secondly, the films were further immersed into a water solution (20 mL) B of PdCl₂ (10 mM, 3.4 mL), and then the films were rinsed with deionized water to obtain the BiVO₄/NiFeOx photoanodes. The water solution (20 mL) C contains NiSO₄·6H₂O (0.15 g), FeO₄·H₂O (0.15 g), NH₄F (0.2 g), NaH₂PO₄·H₂O (0.8 g), and Na₂CO₃·H₂O (2H₂O) (0.4 g), and the value of pH was further adjusted to 9.0 by adding ammonia.54

Measurement and characterization. Scanning electron microscopy measurements were carried out on a field-emission scanning electron microscope (SEM, SU8020). Transmission electron microscopy (TEM) measurements were performed by using a FEI Tecnai TF20 microscope operated at 200 kV. The elemental composition and chemical valence states were explored by X-ray photoelectron spectroscopy (XPS, Al-Kα). The crystalline structures were identified by X-ray diffraction analysis (XRD, Smartlab-SE). UV-visible diffuse reflectance spectra were performed on a UV-2550 spectrophotometer (Shimadzu) by using BaSO₄ as the reference.

Spectrum measurements. The photoluminescence (PL) spectra were tested on F-7000 fluorescence spectrophotometer (Hitachi, Tokyo Japan) at 1.0 eV under AM 1.5 light intensity to 100 mW cm⁻². The element composition and chemical valence states were explored by X-ray photoelectron spectroscopy (XPS, Al-Kα). The crystalline structures were identified by X-ray diffraction analysis (XRD, Smartlab-SE). UV-visible diffuse reflectance spectra were performed on a UV-2550 spectrophotometer (Shimadzu) by using BaSO₄ as the reference.

Photocurrent density. The electrochemical impedance spectroscopy (EIS) Nyquist plots were obtained at 0.75 V (vs. RHE) with a small AC amplitude of 10 mV in the frequency range of 10⁻² to 10⁶ Hz and the measured spectra were fitted with Zview software. Surface charge transfer efficiencies (ηct) of BiVO₄, BiVO₄/NiFeOx, and BiVO₄/NiFeO₄ photoanodes can be calculated using the following equation56:

![](https://doi.org/10.1038/s41467-021-27299-0)

The evolution of H₂ and O₂ was performed in a 0.5 M K₃BO₃ electrolyte at 1.23 V теат under AM 1.5 G illumination (100 mW cm⁻²) by an online gas analysis system (Labosol 6 A, Beijing Perfect light Technology Co. Ltd.) and a gas chromatograph (GC 7890 A, Agilent Technologies).

The PEC performances of two parallel BiVO₄/NiFeO₄ photoanodes (single area: 2 x 3.5 cm², distance: –1 cm) were performed at 1.23 V теат in 0.5 M K₃BO₃. Specifically, the simulated solar light illuminates vertically these two photoanodes, which were connected with copper wires.

Computational method. The Vienna Ab Initio Simulation Package (VASP) code described by the projector augmented wave (PAW) method for ion-electron interaction was applied to the simulation calculations. The generalized gradient approximation (GGA) was used in the form of the Perdew-Burke-Ernzerhof (PBE) functional. The empirical correction scheme of Grimme (DFT-D2) was adopted for considering van der Waals (vdW) interactions. The convergence criterion for Hellmann-Feynman forces and total energy were set to 0.01 eV/A and 10⁻¹ eV, and the vacuum space in the z-direction was greater than 20 Å to avoid the interaction between adjacent units during structural relaxation. A ten atomic layers BiVO₄ (001) slab model was used, and the bottom six atomic layers were fixed to simulate the bulk structure.

Data availability. The data reported in this article are provided in the Source Data file. The remaining data that support the findings of this study are available from the corresponding author upon request. Source data are provided with this paper.

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Author contributions
B.Z. and Y.B. conceived and designed experiments. L.C. and G.L. directed the experiments and revised the paper. B.Z. performed the measurements. S.Y. and Y.D. carried out the theoretical simulation. X.H. performed the XPS measurement and G.D. performed the SEM measurements. B.Z. and Y.B. wrote the paper. All authors reviewed the paper.

Competing interests
The authors declare no competing interests.

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