Enhancing photoelectrochemical water splitting by combining work function tuning and heterojunction engineering

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We herein demonstrate the unusual effectiveness of two strategies in combination to enhance photoelectrochemical water splitting. First, the work function adjustment via molybdenum (Mo) doping significantly reduces the interfacial energy loss and increases the open-circuit photovoltage of bismuth vanadate (BiVO4) photoelectrochemical cells. Second, the creation and optimization of the heterojunction of boron (B) doping carbon nitride (C3N4) and Mo doping BiVO4 to enforce directional charge transfer, accomplished by work function adjustment via B doping for C3N4, substantially boost the charge separation of photo-generated electron-hole pairs at the B-C3N4 and Mo-BiVO4 interface. The synergy between the above efforts have significantly reduced the onset potential, and enhanced charge separation and optical properties of the BiVO4-based photoanode, culminating in achieving a record applied bias photon-to-current efficiency of 2.67% at 0.54 V vs. the reversible hydrogen electrode. This work sheds light on designing and fabricating the semiconductor structures for the next-generation photoelectrodes.
Photocatalytic water splitting is a key technology for future hydrogen production. Despite widespread attention, the efficiency of light harvesting, charge separation and surface Fermi-level pinning still has much room for improvement. Recent efforts have improved the photocurrent density of BIVO₄-based photoanodes from 0.24 V to ~1 V in 10 s irradiation. Second, to further improve the charge separation efficiency at low bias, we elaborated a Bi-C₃N₄/Mo-BIVO₄ photoanode for PEC water splitting. We have significantly increased the light harvesting efficiency (LHE) of the B-C₃N₄/Mo-BIVO₄ photoanode, achieving photocurrent densities of 4.7 mA cm⁻² at 0.6 V vs. RHE (Φₑ_p = 79%) and 6 mA cm⁻² at 1.23 V vs. RHE (Φₑ_p = 98%) in potassium phosphate buffer (PPB) solution with 0.5 M Na₂SO₄ hole scavenger (pH 7). When the NiFeOₓ was anchored on the B-C₃N₄/Mo-BIVO₄ photoanode as an OER catalyst layer forming the NiFeOₓ/B-C₃N₄/Mo-BIVO₄ photoanode, we obtained photocurrent densities of 3.85 mA cm⁻² at 0.54 V vs. RHE (71% IPCE) and 5.93 mA cm⁻² at 1.23 V vs. RHE (92% IPCE) in PPB solution without any hole scavengers such as Na₂SO₄ (pH 7). Significantly, the NiFeOₓ/B-C₃N₄/Mo-BIVO₄ photoanode has achieved an ABPE up to 2.67% at 0.54 V vs. RHE, which is the highest reported to date and yet, with the lowest biased-voltage, for BIVO₄-based PEC devices.

### Results

**Characterization of the NiFeOₓ/B-C₃N₄/Mo-BIVO₄ photoanode.** The XRD patterns collected from BIVO₄, Mo-BIVO₄, B-C₃N₄/Mo-BIVO₄, NiFeOₓ/B-C₃N₄/Mo-BIVO₄ prepared on the F-doped SnO₂ conducting glass (FTO), C₃N₄ and B-C₃N₄ are shown in Supplementary Fig. 1. All of the diffraction peaks in the XRD patterns obtained can be well indexed to monoclinic BIVO₄ (JCPDS PDF #75–1445) and graphite-C₃N₄ (JCPDS PDF #50–1250). As shown in Fig. 1a, the champion photoanode consisted of nanoporous B-C₃N₄/Mo-BIVO₄ heterojunctions in tandem with a NiFeOₓ oxygen evolution catalyst (OEC) layer, which were successfully grown on the FTO substrate. In row, suggesting that the newly-coated B-C₃N₄ has covered the nanoporous Mo-BIVO₄ and NiFeOₓ layer has covered the B-C₃N₄/Mo-BIVO₄ as the OEC. Figures 1h, i is a typical TEM image and a high-resolution TEM (HRTEM) image of the NiFeOₓ/B-C₃N₄/Mo-BIVO₄ sample, respectively, revealing that the B-C₃N₄ and Mo-BIVO₄ are crystallized (Fig. 1j, k) while NiFeOₓ is non-crystallized (Fig. 1l). The lattice fringes of 0.325 nm and 0.254 nm are ascribed to the (002) plane of C₃N₄ and the (020) plane of BIVO₄, respectively.

**Work function tuning.** The first strategy we used to optimize the PEC performance of BIVO₄-based photoanodes, more precisely, to lower the onset potential, was to systematically adjust the work function by Mo doping below 1%, which is a previously uncharted doping regime (the atomic ratio is shown in Supplementary Table 1). Figure 2a compares the linear sweep...
voltammograms (LSV) curves of BiVO₄ (black line), 0.05% Mo
doped BiVO₄ (blue line) and 0.1% Mo doped BiVO₄ (red line)
0.5% Mo doped BiVO₄ (purple line) at a scan rate of 25 mV s⁻¹
in 0.5 M Na₂SO₃ aqueous solution as a hole scavenger with PPB
(pH 7) under AM 1.5 G one-sun illumination. The pure BiVO₄
photoanode achieved photocurrent density of 3.2 (±0.3) mA cm⁻²
at 0.6 V vs. RHE and 4.7 (±0.3) mA cm⁻² at 1.23 V vs. RHE, in
agreement with the previous report⁷. With a slight doping,
the photocurrent density of 0.1% Mo-BiVO₄ increased to 3.4 (±0.2)
mA cm⁻² at 0.6 V vs. RHE and 4.98 (±0.2) mA cm⁻² at 1.23 V vs.
RHE. From our extensive measurements, the photocurrent den-
sities assuming 100% absorbed photon-to-current ef-
fi cie ncy (Jabs) of the BiVO₄-based and the Mo-BiVO₄-based photoanodes were
consistently ~4.7 mA cm⁻² and ~5.01 mA cm⁻², respectively
(Supplementary Fig. 3). The increase in Jabs could be ascribed to the
enhanced LHE, carrier concentration (Supplementary Fig. 27)
and mobility (Supplementary Fig. 28) resulting from the Mo
doping³³–³⁷. More interestingly, the onset potential of Mo doped
BiVO₄ (0.05, 0.1, and 0.5%) photoanodes became significantly
more negative than that of pure BiVO₄ photoanode, and the rapid
photocurrent increase region against bias for the 0.05% and 0.1%
Mo doped BiVO₄ is also more negative than that of the BiVO₄
photoanode. However, the rapid photocurrent increase region
against bias for the 0.5% Mo doped BiVO₄ is more positive than
that of BiVO₄. This phenomenon is caused by the changed open-
circuit photo-voltage (OCP) of BiVO₄ due to the work function
adjustment by the Mo doping.

Supplementary Fig. 5 shows OCP changes of the Mo doped
BiVO₄ (0.05, 0.1, and 0.5%) relative to the pure BiVO₄
photoanode due to the truncation of Fermi-level pinning and
surface trap states of BiVO₄. OCP is essentially the difference
between open-circuit voltage in dark (OCVdark) and light
(OCVlight). The work function is tuned in such a way that the
Fermi level (E_F) is far from CBM when light is off resulting in a
small OCVdark, but when light is on (AM 1.5 G), the quasi-Fermi-
level (E_Fn) becomes as close as possible to CBM giving rise to a
large OCVlight. Consequently, a large OCP (Vph) can be obtained.
Shown in Supplementary Fig. 5 are the OCP timing pro-
fi les of the Mo doped BiVO₄ (0.05, 0.1, and 0.5%) and the pure BiVO₄
photoanodes in PPB solution with the Na₂SO₃ hole scavenger
(pH 7) over a testing interval of 30 s (Supplementary Fig. 5a) and
2000 s (Supplementary Fig. 5b). The most important observation
is that the 0.1% Mo-BiVO₄ photoanode achieved the highest OCP
(~1 V in the first irradiation on/off cycle, and ~0.55 V in the
cycles after testing for 1600 s). These OCP values are much higher
than those of pure-BiVO₄ (~0.35 V and ~0.15 V), 0.05% Mo-
BiVO₄ (~0.8 V and ~0.4 V), and 0.5% Mo-BiVO₄ photoanode
(~0.23 V and ~0.16 V) when tested under otherwise the same
conditions. A higher OCP value means a more favorable driving
force for water oxidation since it determines the difference
between the hole quasi-Fermi-level of the semiconductor
heterojunction and the redox potential of the electrolyte.

The above presented OCP result can be captured by the picture
illustrated in Fig. 2b. For the pure BiVO₄, the Fermi-level position
of ideal BiVO₄ is close the valence band edge of BiVO₄, but the lattice defects formed during synthesis and surface state trapped electrons (V⁴⁺) of pure BiVO₄ move the Eₚ of pure BiVO₄ negatively (Supplementary Fig. 23)³⁸-⁴⁰. When the pure BiVO₄ photoanode was immersed in the solution, the Eₚ of pure BiVO₄ became more positive than the redox potential due to Fermi-level pinning by surface trapped electrons, making the OCV of BiVO₄ relatively high. Meanwhile, under AM 1.5 G illumination, the Fermi-level pinning effect prevented the Eₚ of BiVO₄ from moving very close to the conduction band minimum (CBM) of BiVO₄, leading to a moderate OCV and thus a low OCP (Vph) of pure BiVO₄ very low. Importantly, the Mo doping in BiVO₄ could reduce the surface trap states and at the same time introduced new states, thus moderating the Fermi-level pinning effect (Supplementary Fig. 4)⁴¹. Due to the reduced Fermi-level pinning effect by Mo doping, for the 0.05% and 0.1% Mo-BiVO₄ photoanodes, the Eₚ and Eₜ moved more positive and negative than Eₚ of the pure BiVO₄ photoanode, respectively, thereby enhancing the OCPs. However, for the 0.5% Mo-BiVO₄, new states were introduced due to the excess Mo doping, and the Eₜ became much closer to CBM, leading to high OCV of BiVO₄ (6.8 mA cm⁻²). Thus the moderate Mo doping of BiVO₄ in the low end doping regime can increase the photo-voltage carrier concentration and mobility of the BiVO₄ photoanodes, and improve their onset potential and photocurrent density.

**Heterojunction engineering.** We now turn to our second strategy to optimize the PEC performance of BiVO₄-based photoanodes by further increasing the utilization of Jmax. To accomplish it, we started with the basic C₃N₄/BiVO₄ junction, and then worked up for optimization by B-doping C₃N₄ and the Mo-doping BiVO₄. Both LHE and charge separation have been enhanced, leading to the increase of Jabs and Φsep of the photoanode. Supplementary Fig. 7 shows the UV–vis absorption spectra from the diffuse reflectance measurements. The band gaps of B-C₃N₄ and C₃N₄ were estimated to be 2.41 eV, respectively. Supplementary Fig. 8b is the LHE of B-C₃N₄/Mo-BiVO₄, which exhibits stronger absorption in the range between 300 nm and 500 nm than Mo-BiVO₄. Supplementary Fig. 8c shows the spectra of the solar irradiance of AM 1.5 G (ASTM G173-03) and those weighted by the LHE spectra of B-C₃N₄/Mo-BiVO₄, which shows the Jmax of B-C₃N₄/Mo-BiVO₄ achieved ~6.0 mA cm⁻². Figure 3a compares the LSV curves of 0.1% Mo-BiVO₄ (black line), C₃N₄/Mo-BiVO₄ (cyan line) and B-C₃N₄/Mo-BiVO₄ (purple line) at a scan rate of 25 mV s⁻¹ using 0.5 M Na₂SO₃ as a hole scavenger in a PPB buffered aqueous solution (pH7) under AM 1.5 G illumination. The photocurrent density of B-C₃N₄/Mo-BiVO₄ reached ~6 mA (±0.2) cm⁻² at 1.23 V vs. RHE, and this is higher than that of 0.1% Mo-BiVO₄ (5 mA cm⁻²), at least partly due to the increase in LHE and Jabs after the conjugation with B-C₃N₄. At 0.6 V vs. RHE, the photocurrent density of B-C₃N₄/Mo-BiVO₄ was 4.7 mA cm⁻², which is much higher than that of 0.1% Mo-BiVO₄ (3.4 mA cm⁻²). However, the photocurrent of C₃N₄/Mo-BiVO₄ only achieved 2.9 and 4.2 mA cm⁻² at 0.6 and 1.23 V vs. RHE, which are lower than that of Mo-BiVO₄ (3.4 and 5 mA cm⁻²), although increased LHE and Jabs by compositing C₃N₄ and B-C₃N₄. The results of Φsep of Mo-BiVO₄ (black line), C₃N₄/Mo-BiVO₄ (cyan line) and B-C₃N₄/Mo-BiVO₄ (purple line) clearly shows that B-C₃N₄ decoration can greatly increase the Φsep of Mo-BiVO₄, while pure C₃N₄ decoration will reduce the Φsep of Mo-BiVO₄ (Fig. 3b). The Φsep of B-C₃N₄/Mo-BiVO₄ achieved 79 and 98% at 0.6 V and 1.23 V vs. RHE, respectively. The Φsep of B-C₃N₄/Mo-BiVO₄ at 0.6 V vs. RHE is higher than that of Mo-BiVO₄ (69%), and at 1.23 V vs. RHE, the Φsep of Mo-BiVO₄ and B-C₃N₄/Mo-BiVO₄ are achieved near 100% cause the charge separation of Mo-BiVO₄ and B-C₃N₄/Mo-BiVO₄ have reached their limits at higher bias voltage. However, the Φsep of C₃N₄/Mo-BiVO₄ only achieved 60 and 80% at 0.6 V and 1.23 V vs. RHE, which are even lower than that of Mo-BiVO₄. This result shows that when C₃N₄ is compositing the Mo-BiVO₄, it has no effect on the separation of the photo-generated charges. These results mean that although the thermodynamic potential of pure C₃N₄ and BiVO₄ are match, the heterojunction of pure C₃N₄ and Mo-BiVO₄ became a compound center of photo-generated charge. As shown in Fig. 3c, d, when the Mo-BiVO₄ and pure C₃N₄ are in contact, the O1s and V2p positive shift 0.34 eV and N1s negative shifts 0.96 eV. Supplementary Fig. 9 shows the CBM, VBM and Fermi level of BiVO₄, Mo-BiVO₄, C₃N₄ and B-C₃N₄ by UPS and XPS VB spectra data (Supplementary Figs. 10, 11, 12, and 13). The Fermi level of BiVO₄ and Mo-BiVO₄ are in the middle of their band gap (BiVO₄: 1.21 eV and Mo-BiVO₄: 1.16 eV) and the Fermi level of B-C₃N₄ is close to its VBM, and the Fermi level of pure C₃N₄ is close to its CBM. The DFT data
In detail, when Mo-BiVO₄ and C₃N₄ come into contact to form a heterojunction, the bands on the two sides bend oppositely into the Fermi level of C₃N₄ is getting closer to the VBM generated charges. On the other hand, due to the B element doping, the Fermi level of B-C₃N₄ is getting closer to the VBM generated charges. Supplementary Fig. 15 displays the correct charge transfer direction, which will increase the separation efficiency (Φsep) of C₃N₄/Mo-BiVO₄, 0.1% Mo-BiVO₄ and B-C₃N₄/Mo-BiVO₄. XPS core-level shifts of the peaks at 362 cm⁻¹ and 702 cm⁻¹ are attributed to the V-O vibration of the Mo-BiVO₄. The Raman peaks of B-C₃N₄ are in contact, a cliff like junction is formed with the spike-like structure (Fig.3e), and thus the electrons from the C₃N₄ side can hardly transfer to the Mo-BiVO₄ side. The holes energy barrier at the interface. Therefore, the contact interface of Mo-BiVO₄ and B-C₃N₄ is chemically linked to Mo-BiVO₄.

PEC water splitting performance. In order to use the B-C₃N₄/Mo-BiVO₄ photoanode for PEC water splitting in solution without hole scavenger, the NiFeOₓ layer was used as an OEC material, which was deposited on the photo-active area of B-C₃N₄/Mo-BiVO₄ photoanode surface by photoelectrodeposition method. Supplementary Figs. 16 and 17 show the XPS data of Ni, N, B, C, Bi, Mo, O, and Fe. For B-doped C₃N₄ as can be seen from Supplementary Figs. 16c, the peak of B is located at around 191.9 eV, fairly close to the binding energy of B in the –C–N–B– and –N–B–(N)₂– groups (192.1 eV) of the B-C₃N₄ materials reported in the literature. The oxidation state of B is consistent with the results of B-doped C₃N₄ in the reported literature. As shown in Fig. 4a and Supplementary Fig. 21, the PEC water splitting capability of NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode (orange solid line) achieves 4.18 mA cm⁻² and 5.93 (±0.3) mA cm⁻² at 0.6 V vs. RHE and 1.23 V vs. RHE in PPB solution (pH 7), which are much higher than that of Mo-BiVO₄ photoanode and B-C₃N₄/Mo-BiVO₄. Meanwhile, the photocurrent density of NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode at 0.6 V vs. RHE and 1.23 V vs. RHE are much close to that of NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode (orange dotted line) in PPB solution with Na₂SO₃ hole scavenger (pH 7, 2.46 V vs. RHE).
4.37 (±0.3) mA cm$^{-2}$ and 5.96 (±0.3) mA cm$^{-2}$). Supplementary Fig. 18 shows that the B-C$_3$N$_4$ can not only increase the photocurrent density in the low biased-voltage range (0.1–0.8 V vs. RHE) by increasing the separation efficiency of photoanode, but also increase the photocurrent density in the high biased-voltage range (0.8–1.3 V vs. RHE). The IPCEs of NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$, NiFeO$_x$/Mo-BiVO$_4$, NiFeO$_x$/BiVO$_4$, B-C$_3$N$_4$/Mo-BiVO$_4$, Mo-BiVO$_4$, and BiVO$_4$ at 0.54 V vs. RHE in PPB solution (pH 7), which shows that the B-C$_3$N$_4$ can increase the charge separation efficiency and light absorption of photoanode. On the other hand, the NiFeO$_x$ cannot increase light absorption of photoanode, and it only plays the role of a co-catalyst (OEC) here (Supplementary Fig. 19). In Fig. 4b, due to the high oxygen evolution reaction capacity of NiFeO$_x$, the dark LSV of NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode shows a remarkable cathodic shift (~340 mV) of onset potential compared to B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode and Mo-BiVO$_4$ photoanode. However, the LSV curves of the B-C$_3$N$_4$/Mo-BiVO$_4$ and NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ recorded at a scan rate of 25 mV s$^{-1}$ in PPB solution with Na$_2$SO$_3$ as a hole scavenger (pH 7), which shows that the photocurrent density of samples measured in solution with Na$_2$SO$_3$ will decline after the NiFeO$_x$ layer deposition (Supplementary Fig. 20). Figure 4c shows the half-cell applied bias photon-to-current efficiency (ABPE) of the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode. The ABPE is calculated to be 2.67% at 0.54 V vs. RHE, which is the highest recorded for BiVO$_4$ based photoanodes (Fig. 6c). Evidently, the highest efficiency has been achieved for the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode at the lowest potential (0.54 V vs. RHE) among the previously reported values, which shows the highest performance of PEC water splitting for BiVO$_4$ based photoanodes. Shown in Supplementary Figs. 25 and 26 are the LSV curves and ABPE measurement results in the two electrodes configuration (NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode and Pt cathode) in PPB solution (pH 7). It can be seen that the ABPE of whole PEC system (without reference electrode) achieved 2.1% at 0.62 V vs. Pt. Figure 4d shows the incident-photon-to-current conversion efficiency (IPCE) and the absorbed photon-to-current efficiency (APCE) spectra of NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode at 0.54 V vs. RHE and 1.23 V vs. RHE in PPB solution (pH 7). The maximum IPCE value of NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode reaches ~71 and 92% at 0.54 V vs. RHE and 1.23 V vs. RHE. The APCE of NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode reaches ~100% at 1.23 V vs. RHE, establishing the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode used all the light it could absorb for PEC water splitting at 1.23 V vs. RHE. Therefore, these results clearly show that the NiFeO$_x$ OEC can greatly improve the PEC capacity of B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode in the absence of any hole scavenger.

As shown in Fig. 5 and Supplementary Video 1, the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode exhibits excellent operational stability for half-cell PEC water splitting in PPB solution (pH 7) at 0.54 V vs. RHE under AM 1.5 G irradiation. Figure 5a shows the photograph of the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode half-cell PEC water splitting system, and Fig. 5b–d show the photographs of the photoanode, the Pt cathode and the Ag/AgCl reference electrode separately. The chronoamperometry curve of the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode was collected at 0.54 V vs. RHE in 10 h. The photocurrent density of the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode was initially 3.85 mA cm$^{-2}$ and decreased by only 10% after 10 h of operation, demonstrating the good stability of the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode during the long time irradiation in PPB solution (Fig. 5e). And the photocurrent densities of the NiFeO$_x$/Mo-BiVO$_4$ and NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanodes decayed by 5 and 8% (Supplementary Fig. 24), respectively, very close to the stability testing result of the NiFeO$_x$/B-C$_3$N$_4$/Mo-BiVO$_4$ photoanode at 0.54 V vs. RHE. These results confirm that the NiFeO$_x$ is a stable co-catalyst for the BiVO$_4$-based photoanodes, essentially consistent with the recent reports. The generation rates of H$_2$ and O$_2$ by our half-cell system are measured to be 77.5 μM h$^{-1}$ and 336 μM h$^{-1}$, respectively, with Faradic efficiency of 98% (Fig. 5f).
ABPE are the highest recorded for BiVO₄-based NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode at 0.54 V vs. RHE; dashed curves indicate the H₂ and O₂ evolution with 98% Faraday efficiency. Under a fairly low bias-voltage (0.54 V vs. RHE), which shows the highest efficiency of 2.67% ABPE with a fairly high photocurrent density of 3.85 mA cm⁻², ABPE of 2.67% and IPCE of 71% at 0.54 V vs. RHE, which are the highest yet reported with the lowest biased-voltage for BiVO₄-based PEC materials. The NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode exhibited significantly enhanced PEC activity for water splitting by systematically work function adjustment (Fig. 6a). We have demonstrated the work function adjustment via Mo doping could reduce the interfacial energy loss and increase the open-circuit photo-voltage of BiVO₄ PEC cells. In addition, the creation and optimization of the heterojunction (p-n) of B-C₃N₄ and Mo-BiVO₄ with correct charge transfer direction were accomplished by work function adjustment via B doping for C₃N₄, thereby increasing the separation of photo-generated electron-hole pairs at the B-C₃N₄ and Mo-BiVO₄ interface (Fig. 6a, b). The data of DFT calculation, XPS and UPS confirm the Fermi level and band shift of B-C₃N₄ and Mo-BiVO₄. This synergistic effect between B doping of C₃N₄ and Mo doping of BiVO₄ with the NiFeOₓ OEC has allowed the NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode to achieve the record efficiency of 2.67% ABPE with a fairly low bias-voltage (0.54 V vs. RHE), which shows the efficiency of ABPE are the highest recorded for BiVO₄-based photoanodes. The demonstration of the NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode with excellent PEC water splitting capability achieved by the synergistic combination of work function tuning and heterojunction deliberation will inform the design and development of the next-generation PEC materials and devices.

**Discussion**

In conclusion, the NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode has provided an archetype to exploit the potential of boosting the photoelectrochemical performance by the synergistic combination of work function tuning and heterojunction construction. The bespoke photoanode achieved a remarkable photocurrent density of 3.85 mA cm⁻², ABPE of 2.67% and IPCE of 71% at 0.54 V vs. RHE, which are the highest yet reported with the lowest biased-voltage for BiVO₄-based PEC materials. The NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode exhibited significantly enhanced PEC activity for water splitting by systematically work function adjustment (Fig. 6a). We have demonstrated the work function adjustment via Mo doping could reduce the interfacial energy loss and increase the open-circuit photo-voltage of BiVO₄ PEC cells. In addition, the creation and optimization of the heterojunction (p-n) of B-C₃N₄ and Mo-BiVO₄ with correct charge transfer direction were accomplished by work function adjustment via B doping for C₃N₄, thereby increasing the separation of photo-generated electron-hole pairs at the B-C₃N₄ and Mo-BiVO₄ interface (Fig. 6a, b). The data of DFT calculation, XPS and UPS confirm the Fermi level and band shift of B-C₃N₄ and Mo-BiVO₄. This synergistic effect between B doping of C₃N₄ and Mo doping of BiVO₄ with the NiFeOₓ OEC has allowed the NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode to achieve the record efficiency of 2.67% ABPE with a fairly low bias-voltage (0.54 V vs. RHE), which shows the efficiency of ABPE are the highest recorded for BiVO₄-based photoanodes. The demonstration of the NiFeOₓ/B-C₃N₄/Mo-BiVO₄ photoanode with excellent PEC water splitting capability achieved by the synergistic combination of work function tuning and heterojunction deliberation will inform the design and development of the next-generation PEC materials and devices.

**Methods**

**Preparation of BiVO₄ and Mo-BiVO₄ electrode.** BiVO₄ photoanodes were fabricated by a two-step process via a modified method which was originally developed by Kim and Chó. At first, a template-free electrochemical deposition was applied to prepare the BiOI nanosheets using a conventional three-electrode glass cell, where a piece of F-doped SnO₂ coated glass (FTO, Nippon Sheet Glass, 1 × 2 cm) served as the working electrode, a Pt electrode served as the counter electrode and an Ag/AgCl electrode served as the reference electrode. Generally, 30 mL of solution containing 0.4 M KI (99.0%, Tianjin Zhiyan Reagent Co. Ltd.) and 0.04 M Bi(NO₃)₃ (99.0%, Shanghai Macklin Biochemical Co. Ltd) was adjusted pH to 1.7 by adding HNO₃ (65–68%, AR, Guangzhou Chemical Reagent). Then, 20 mL of absolute ethanol (100%) containing 0.23 M p-benzoquinone (97%, Aladdin) was mixed into the above solution and vigorously stirred for several minutes. Cathodic deposition of BiOI (1 × 1 cm area) was performed potentiostatically in the final solution at −0.1 V vs. Ag/AgCl at room temperature (RT) for 200 s. The second step was the conversion of BiOI to BiVO₄. Dimethyl sulfoxide (DMSO, AR, Tianjin Damao Reagent) solution containing 0.2 M vanadyl acetylacetonate (VO(acac)₂, 95%, Aladdin) was impregnated on BiOI electrodes (50 μL) and then annealed in air at 450 °C for 2 h with ramping rate of 2 °C min⁻¹. Lastly, the BiVO₄ electrodes were soaked in 1 M NaOH (AR, Guangzhou Chemical Reagent) solution for 1 h with gentle stirring to remove the excess V₂O₅. The obtained pure BiVO₄ electrodes were rinsed by deionizer water and dried at RT.

Molybdenum doped BiVO₄ (Mo-BiVO₄) photoanodes were prepared in the same way by adding Na₂MoO₄ as the Mo source. In detail, 1, 2, and 10 μL of 0.1 M Na₂MoO₄ (AR, Tianjin Damao Reagent) aqueous solution was added into 1 mL of the above VO(acac)₂ DMSO solution before it was impregnated on BiOI electrodes.
The corresponding concentration ratio of Mo/Bi was 0.05%, 0.1%, and 0.5%, respectively.

Preparation of C3N4 and B-C3N4. The bulk graphite-C3N4 (C3N4) was fabricated by directly heating low-cost melamine (99%, Aladdin). In detail, 5 g melamine powder was placed in an alumina crucible with a cover, then heated to 500 °C for 2 h in a muffle furnace with a heating rate of 2 °C min−1. The obtained bulk C3N4 was grinded into small powder, and 100 mg C3N4 powder was dispersed in 100 mL isopropyl alcohol (AR, Tianjin Damao Reagent) and exfoliated by ultrasonication for 24 h to obtain C3N4 nanosheets (C3N4-NS). The resultant dispersion was centrifuged at 3000 rpm for 10 min, and the supernatant containing exfoliated C3N4-NS was collected by pipette. Boron doped C3N4 nanosheets (B-C3N4-NS) supernatants were prepared in the same way but heating the mixture of 0.5 g boric acid (GR, Aladdin) and 5 g melamine.

Preparation of C3N4-NS/BiVO4 and B-C3N4-NS/Mo-BiVO4 electrode. The BiVO4 or Mo-BiVO4 photoanodes were immersed into 20 mL C3N4-NS or B-C3N4-NS supernatants for 1 h. After rinsed with deionized water, the obtained (B-)C3N4/ (Mo-)BiVO4 photoanodes were annealed at 350 °C in air for 1 h for better combination.

Photoelectrodeposition of NiFeOx OEC layer. NiFeOx OEC layer was synthesized using a simple photoelectrodeposition method reported. NiFeOx layer was photoelectrodeposited on the B-C3N4/Mo-BiVO4 in 0.4 M FeSO4 and 0.04 M NiSO4 solution at 0.6 V vs. Ag/AgCl (total charge 100 mC/cm2) at RT. The NiFeOx/B-C3N4/Mo-BiVO4 electrode was then washed with deionizer water and dried in air at 60 °C.

Analysis. The as-synthesized products were characterized by a scanning electron microscope (SEM, Zeiss G-500), transmission electron microscope (TEM, JEM 2100 F, FEI Tecnai G2F30), X-Ray Diffractometer (XRD, D8 ADVANCE), X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS, Thermo Fisher Scientific ESCALab250) and Raman spectroscopy (Renishaw inVia). The optical properties of the products were measured with an UV–vis–NIR Spectrophotometer (UV–vis–NIR, Shimadzu UV-2450).

Photoelectrochemical and electrochemical measurements. All the PEC and electrochemical measurements were carried out in a three-electrode cell with a flat quartz window to facilitate illumination of the photoelectrode surface. The working electrode is the product fabricated in this work, while Pt electrode was used as a counter electrode and Ag/AgCl electrode was used as a reference electrode, respectively. The illumination source was AM 1.5 G solar simulator (Newport 69920, 1000 W xenon lamp), coupled with an infrared water filter (Oriel 6127) and aligned monochromator (Oriel Cornerstone 130 1/8 m). All the electrochemical measurements were performed on an SP-150 electrochemical workstation (SP-150, Bio-Logic SAS, France) at RT. More PEC and electrochemical calculations are shown in the Supporting information.

Data availability
The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data are available from the corresponding author upon request. All relevant data are available from the authors upon reasonable request.

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