Simultaneous enhancements in photon absorption and charge transport of bismuth vanadate photoanodes for solar water splitting

Tae Woo Kim¹, Yuan Ping², Giulia A. Galli³ & Kyoung-Shin Choi¹

n-Type bismuth vanadate has been identified as one of the most promising photoanodes for use in a water-splitting photoelectrochemical cell. The major limitation of BiVO₄ is its relatively wide bandgap (~2.5 eV), which fundamentally limits its solar-to-hydrogen conversion efficiency. Here we show that annealing nanoporous bismuth vanadate electrodes at 350 °C under nitrogen flow can result in nitrogen doping and generation of oxygen vacancies. This gentle nitrogen treatment not only effectively reduces the bandgap by ~0.2 eV but also increases the majority carrier density and mobility, enhancing electron–hole separation. The effect of nitrogen incorporation and oxygen vacancies on the electronic band structure and charge transport of bismuth vanadate are systematically elucidated by ab initio calculations. Owing to simultaneous enhancements in photon absorption and charge transport, the applied bias photon-to-current efficiency of nitrogen-treated BiVO₄ for solar water splitting exceeds 2%, a record for a single oxide photon absorber, to the best of our knowledge.

¹ Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA. ² Department of Chemistry, University of California, Davis, California 95616, USA. ³ Institute for Molecular Engineering, University of Chicago, Chicago, Illinois 60637, USA. † Present address: Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA; California Institute of Technology, Pasadena, California 91125, USA. Correspondence and requests for materials should be addressed to G.A.G. (email: gagalli@uchicago.edu) or to K.-S.C. (email: kschoi@chem.wisc.edu).
The major challenge for solar hydrogen production is the reduction of hydrogen production cost comparable to that of fossil-based fuels. To make solar hydrogen production a reality, a significant cost reduction for the construction of a photoelectrochemical cell (PEC) is critical. Among various semiconductor electrodes (photoelectrodes) for use in PECs, oxide-based photoelectrodes have the possibility of significantly lowering the materials and processing costs while being stable in aqueous media. N-type bismuth vanadate (BiVO₄) has recently emerged as one of the most promising photoanodes for use in water-splitting PECs. It absorbs a substantial portion of the visible spectrum (bandgap energy, ~2.5 eV) and has a favourable conduction band edge position, which is very near the thermodynamic H₂ evolution potential. As a result, it demonstrated the most negative photocurrent onset potential for water oxidation among all n-type semiconductors (photoanodes) having bandgaps in the visible region. Also, it appears to be fairly stable against chemical and photoelectrochemical corrosion. A recent report shows that photovoltaic performance of oxide-based photoanodes, nanoporous BiVO₄ electrodes coupled with FeOOH and NiOOH as oxygen evolution catalysts, can achieve an applied bias photon-to-current efficiency (ABPE) for water splitting as high as 1.7% in a stable manner (equation for ABPE is shown in Supplementary Information). This result demonstrated the possibility for constructing a PEC for water splitting using only inexpensive and easy-to-process oxide components.

One of the major limitations of BiVO₄ for further improving the solar energy conversion efficiency is its bandgap (~2.5 eV), which fundamentally limits photon absorption. Considering that there are a substantial number of photons in the 2.0–2.5 eV region, a reduction in bandgap by even 0.1–0.3 eV can result in a significant efficiency increase. As a result, the demonstration of a method for nitrogen doping of BiVO₄ has recently emerged as one of the most promising methods for improving the performance of BiVO₄ electrodes. Nitrogen doping of BiVO₄ was achieved by annealing the BiVO₄ electrodes at 350°C for 2 h while flowing N₂. This is an exceptionally gentle procedure for nitrogen doping considering that nitridation or nitrogen doping of oxides is generally achieved by annealing with a flow of NH₃ at much higher temperatures (~500°C). Annealing under N₂ flow may create oxygen deficiencies in oxide compounds but is usually considered insufficient for nitrogen doping. We believe that the nanoparticulate nature of the BiVO₄ electrodes played a role in enabling nitrogen doping under such mild conditions.

The scanning electron microscopy images and X-ray diffraction studies of N₂-treated BiVO₄ electrodes do not show noticeable changes from those of untreated BiVO₄. The slight increase in bandgap transition can be explained by the incorporation of nitrogen into the BiVO₄ lattice. The maximum photocurrent (Jmax) will increase from 6.47 to 9.12 mA cm⁻² assuming 100% incident photon-to-current conversion efficiency (IPCE) for the photons that enable bandgap transition. However, most previous doping studies of BiVO₄ were to increase carrier densities. Studies reporting the change in photon absorption of BiVO₄ have been scarce and no clear elucidation of the effect of the dopants on the electronic structure and charge transport of BiVO₄ are systematically elucidated by ab initio calculations, which corroborate well with the experimental results. Owing to the advantage in photon absorption, carrier density and carrier mobility, the N₂-treated BiVO₄ electrode, when paired with oxygen evolution catalysts, breaks the wall of 2% ABPE for solar water splitting, a first for a single oxide photoelectrode.

Results
Synthesis and characterization. Nanoporous BiVO₄ electrodes were first prepared by the method described in a recent study, which involves electrochemical deposition of BiOI followed by thermal and chemical conversion to BiVO₄. Nitrogen doping of BiVO₄ was achieved by annealing the BiVO₄ electrodes at 350°C for 2 h while flowing N₂. This is an exceptionally gentle procedure for nitrogen doping considering that nitridation or nitrogen doping of oxides is generally achieved by annealing with a flow of NH₃ at much higher temperatures (~500°C). Annealing under N₂ flow may create oxygen deficiencies in oxide compounds but is usually considered insufficient for nitrogen doping. We believe that the nanoparticulate nature of the BiVO₄ electrodes played a role in enabling nitrogen doping under such mild conditions.

The incorporation of nitrogen into the BiVO₄ lattice was confirmed by electron probe microanalyzer (EPMA) and X-ray photoelectron spectroscopy (XPS). For charge-balanced incorporation of nitrogen, three O³⁻ ions need to be removed for every two N³⁻ ions, creating one oxygen vacancy. Therefore, the formula of nitrogen-doped BiVO₄ can be written as BiVO₄₋₁.₅xNₓ if no other types of oxygen vacancies are present. The EPMA result showed that x is 0.31 ± 0.05 (that is, BiVO₄₋₁.₅xNₓ). XPS study also confirmed the presence of nitrogen in the BiVO₄ lattice by showing a N 1s peak (Fig. 2a) with the nitrogen content, x, estimated to be 0.34 ± 0.02, which is comparable to the value obtained by EPMA. The location of the N 1s peak (397–402 eV) agrees well with that of nitrogen incorporated into the oxide lattice. The incorporation of N into the BiVO₄ lattice was further confirmed by Raman spectra that show significant broadening of various V–O stretching and vibration modes.

Figure 1 | SEM images and photographs. Top-view and side-view SEM images of (a,c) BiVO₄ and (b,d) N₂-treated BiVO₄. Photographs of a water droplet placed on (e) BiVO₄ electrode and (f) N₂-treated BiVO₄ electrode. Scale bars, 1 μm for (a,b) and 200 nm for (c,d).
VO$_3^-$ deformation modes of the bulk sample (Supplementary Fig. 2)$^{27,28}$. This indicates that unlike other oxides, nitrogen incorporation into BiVO$_4$ can occur using N$_2$ as the N source at mild temperatures. In fact, there exist two previous studies reporting nitrogen incorporation into vanadium oxides by annealing under N$_2$ flow$^{29,30}$, suggesting relatively easy nitrogen incorporation into vanadium-based oxides. The XPS study also revealed that the Bi 4f and V 2p peaks of N$_2$-treated BiVO$_4$ were shifted to the lower binding energy (Fig. 2b,c). This should be due to the changes in local coordination environments of Bi and V ions, including a change in ligand type (O to N) and a decrease in coordination number due to oxygen vacancies compensating the charge difference between O$^{2-}$ and N$^{3-}$. In addition, the possibility that the N$_2$ treatment created additional oxygen vacancies$^{31,32}$, which would result in partial reduction of Bi$^{3+}$ and V$^{5+}$ ions, cannot be excluded.

The ultraviolet–visible spectra of BiVO$_4$ and N$_2$-treated BiVO$_4$ electrodes are shown in Fig. 3a. The N$_2$-treated sample clearly showed a shift of the bandgap absorption to lower energy compared with untreated BiVO$_4$. This agrees well with the darker yellow colour of the N$_2$-treated BiVO$_4$ (Fig. 3a, inset). The N$_2$-treated BiVO$_4$ also shows a significant absorption before the absorption edge (wavelength $>$ 550 nm). This is most likely due to N$_2$ treatment generating significant disorder in the atomic arrangement (for example, O defects) on the surface of the high surface area nanoporous BiVO$_4$ electrode while incorporating nitrogen, creating interband states in the bandgap region$^{33,34}$. The absorption due to these interband states makes it difficult to accurately assess the onset for the bandgap transition.

**Photo-oxidation of sulfite** To determine the onset of photon absorption that contributes to the photocurrent generation, wavelength-dependent photocurrent was measured using monochromatic light for the photo-oxidation of sulfite and the IPCE was calculated. Since the oxidation kinetics of sulfite is fast, surface electron–hole recombination is negligible during photo-oxidation of sulfite. Therefore, photo-oxidation of sulfite enables a more precise estimation of photocurrent onset compared with photo-oxidation of water which typically suffers from slow oxidation kinetics and surface recombination.

The IPCE result obtained at 0.6 V versus reversible hydrogen electrode (RHE) shows that the photocurrent onset of the N$_2$-treated sample lies between 540 and 550 nm ($\sim$ 2.27 eV) while that of the untreated sample lies between 500 and 510 nm ($\sim$ 2.46 eV), which indicates a bandgap reduction of ~0.2 eV for the N$_2$-treated sample (Fig. 3b). The J−V plots of BiVO$_4$ and N$_2$-treated BiVO$_4$ obtained using AM 1.5G illumination for sulfite oxidation are also shown in Fig. 3c. The N$_2$-treated BiVO$_4$ electrode shows a significantly higher photocurrent than the BiVO$_4$ electrode.

**Figure 2** XPS of BiVO$_4$ and N$_2$-treated BiVO$_4$. (a) 1s peaks of N, (b) 4f peaks of Bi and (c) 2p peaks of V for BiVO$_4$ (black) and N$_2$-treated BiVO$_4$ (red).

**Figure 3** Optical and photoelectrochemical properties. (a) Ultraviolet–visible absorption spectra with photographs of samples, (b) IPCE at 0.6 V versus RHE, (c) J−V plots for sulfite oxidation under AM 1.5G, 100 mW cm$^{-2}$ illumination (scan rate, 10 mV s$^{-1}$), (d) APCE at 0.6 V versus RHE and (e) $\phi_{\text{sep}}$ calculated from the J−V plots for BiVO$_4$ (black) and N$_2$-treated BiVO$_4$ (red). A 0.5 M phosphate buffer (pH 7.2) containing 1 M Na$_2$SO$_3$ was used as the electrolyte. The error bars were obtained by taking the s.d. values of measurements on three different samples.
potential, corresponding to a 27% increase. This is the first example showing the generation of photocurrent higher than 4 mA cm\(^{-2}\) for any photo-oxidation reaction by any photoanode reported to date at a potential as low as 0.6 V versus RHE.

If the photocurrent enhancement is due only to the enhanced photon absorption by the bandgap reduction, the N\(_2\)-treated sample should show an increase in IPCE but not in the absorbed photon-to-current conversion efficiency (APCE). However, the N\(_2\)-treated sample showed a considerable enhancement in APCE, particularly between 470 and 550 nm (Fig. 3d), indicating that the N\(_2\) treatment also improved electron–hole separation. Indeed, the electron–hole separation yield, \(\phi_{sep}\), of the N\(_2\)-treated sample, which was calculated from the \(J–V\) plots obtained for sulfite oxidation, shows about an 8–10% increase at \(E > 0.45\) V versus RHE (Fig. 3e). For example, the electron–hole separation yields at 0.6 V versus RHE are 0.70 ± 0.04 and 0.76 ± 0.07 for untreated and N\(_2\)-treated BiVO\(_4\), respectively. This means that the 27% photocurrent enhancement observed at 0.6 V for the N\(_2\)-treated sample is partially due to an increase in photon absorption and partially due to an increase in electron–hole separation (see the Methods section and Supplementary Table 1 for detailed calculations).

One plausible mechanism for N\(_2\) treatment to increase \(\phi_{sep}\) is to increase the carrier density by creating extra oxygen vacancies, which can serve as donors, in addition to the oxygen vacancies created for charge-balanced substitution of N\(^{3–}\) with O\(^{2–}\). This can result in an improvement in electron transport and, therefore, in electron–hole separation. The carrier densities in BiVO\(_4\) and N\(_2\)-treated BiVO\(_4\) electrodes were compared by obtaining Mott–Schottky plots (Supplementary Fig. 3). For nanoporous films, since the regions that contribute to space-charge layer capacitance and the corresponding surface area cannot be precisely quantified, accurate quantitative analysis of carrier density using Mott–Schottky analysis is not possible. However, since the samples compared in this study have exactly the same morphologies (particle sizes, aggregations and connectivities), relative qualitative comparison of carrier densities should be possible by comparing the magnitude of the slopes. The result shows that the slope of N\(_2\)-treated BiVO\(_4\) is \(\sim 1/17\) of the slope of BiVO\(_4\), indicating that the N\(_2\)-treated BiVO\(_4\) electrodes possess extra oxygen vacancies that serve as electron donors. This suggests that the record-high photocurrent shown in Fig. 3c is due to improved electron transport properties as well as bandgap reduction.

An increase in n-type carrier density should result in a shift of flatband potential (\(E_{FB}\)) to the negative direction. However, both the photocurrent onset and the \(E_{FB}\) of the N\(_2\)-treated sample are more positive than those of BiVO\(_4\) (Fig. 3c; Supplementary Fig. 3). This is because the Helmholtz layer potential drop (\(V_{HL}\)) of the N\(_2\)-treated BiVO\(_4\) electrode, which is another factor that affects the position of \(E_{FB}\) (ref. 35), is more positive than that of BiVO\(_4\), which is indicated by zeta potential measurements (Supplementary Fig. 4). The change in \(V_{HL}\) of the N\(_2\)-treated sample appears to cancel out the effect of an increased donor density on \(E_{FB}\).

**Density functional theory calculations.** The effect of charge-balanced N incorporation (that is, replacing three O\(^{2–}\) with two N\(^{3–}\)) and of oxygen vacancies on the electronic band structure of BiVO\(_4\) were studied using density functional theory (DFT) calculations, to gain insights into the changes occurring in BiVO\(_4\) upon nitridation. Our experimental results show that in the N\(_2\)-treated BiVO\(_4\), both N substitution and O vacancies are present at the same time, yielding a complex, combined effect on the electronic structure of BiVO\(_4\). Before investigating such combined effect, we discuss the electronic properties of N substitution and oxygen vacancies separately.

We first performed spin-polarized calculations without addressing the charge imbalance between O\(^{2–}\) and N\(^{3–}\). We used the Perdew–Burke–Ernzerh (PBE)\(^{36}\) exchange correlation functional for pure BiVO\(_4\) and BiVO\(_4\) with 12.5% neutral O replaced with neutral N (1:1 substitution). We found that in the presence of N the bandgap of BiVO\(_4\) was reduced by 0.5 eV (Supplementary Fig. 5), mainly because of the hybridization of N and O 2p states close to VBM. The presence of extra holes due to N substitution leads to two localized empty bands (level labelled ‘a’ in Supplementary Fig. 5b) inside the bandgap of BiVO\(_4\). These bands will no longer be present when N substitution accompanies charge-balancing O vacancies, which will serve as electron donors and compensate for excess holes from N substitution, as discussed below (see also Supplementary Fig. 6 for the effect of artificially adding an electron per nitrogen to compensate for the excess holes from N substitution).

To understand the effect of O vacancies separately, we performed spin-polarized calculations at two different oxygen concentrations of 6 and 1.5%, using PBE and PBE with Hubbard U corrections\(^{37}\) (PBE + U, effective \(U(V) = 2.7\) eV\(^{17}\)), to verify the robustness of our results with respect to the functional adopted in our calculations. Both at the PBE and PBE + U levels of theory, at the two concentrations, we found that the presence of O vacancies, which were created by removing neutral O atoms, did not lead to any modification of the bandgap of BiVO\(_4\) (for details see Supplementary Figs 7 and 8). We also observed the formation of localized, filled states inside the bandgap of pristine BiVO\(_4\). Interestingly, the spin density of the gap states is localized on V, as shown in Supplementary Fig. 8, causing local lattice distortions (in addition to those induced by missing O atoms), and indicating the formation of small polarons. Indeed, small polarons are likely to form in oxides such as BiVO\(_4\) that exhibit strong electron–phonon interaction, as indicated, for example, by the large difference between the high frequency and static dielectric constants \(\varepsilon\) (the high frequency and static \(\varepsilon\), averaged over the three lattice directions, are 6.9 and 52, respectively, as computed by density functional perturbation theory\(^{38}\) for pure BiVO\(_4\)).

Our results on the formation of small polarons are consistent with recent mobility measurements on single crystal n-type BiVO\(_4\), which reported very low electron mobilities\(^{39}\) (\(\sim 0.2\) cm\(^{-2}\) V\(^{-1}\) s\(^{-1}\)) and suggested that the conduction of electrons is dominated by small polaron hopping. Previous calculations showed that O vacancies lead to shallow donor levels in BiVO\(_4\) (ref. 31), with negative ionization energies for \(E(V^0/V^2+)\) and that the only stable charged state for an O vacancy in BiVO\(_4\) is \(q = +2\) due to the spontaneous ionization of two electrons, regardless of the Fermi level position\(^{40}\). These results are consistent with our finding that the two electrons present at an O vacancy site are ionized and localized at V atoms, thus forming small polarons. Similar findings for SrTiO\(_3\) have also been discussed in a recent study by Janotti et al.\(^{41}\) We also computed the small polaron binding energy\(^{42}\), that is, the energy difference between bound small polarons and free carriers. We found a non-negligible value of \(\sim 0.50\) eV indicating that the formation of small polarons is energetically favourable (see Methods for calculation details).

Having established the separate effects of N substitution and O vacancies on the electronic structure of BiVO\(_4\), we now turn to analyze their combined effect. In the case of charge-balanced N substitution (9% O replaced with 6% N and 3% O vacancy) we found that no states are formed in the bandgap of BiVO\(_4\), as shown in Fig. 4a. This is because the electrons ionized from O vacancies compensate for the holes generated by N substitution.
thus balancing the charge. No small polaron is formed at the vanadium sites in this case. The important finding is that the bandgap is still lowered by 0.3–0.4 eV (depending on the location in the lattice of the substituted N) compared to that of pure BiVO₄. The computed projected density of states (as shown in Supplementary Fig. 9) showed that the VBM has contributions from both O and N 2p states, similar to the case of N substitution discussed earlier. With lower doping concentration (4.5% O replaced with 3% N and 1.5% O vacancy), the VBM moves upward by 0.2 eV compared with that of pure BiVO₄. In sum, we found that in the presence of N substitution and charge-compensating O vacancies, the bandgap decrease is similar to that obtained in the case where only substitutional N is present, and the bandgap decrease is more pronounced with increasing N concentration.

The information on energy levels provided by band structure calculations is insufficient to investigate light absorption efficiency of BiVO₄. Hence, we also computed the optical transition probabilities from valence to conduction states for pristine and charge-balanced N-doped BiVO₄ (9% O replaced with 6% N and 3% O vacancy) and simulated absorption spectra using the random phase approximation including local field effects. Although this approximation neglects excitonic effects, we expect it to be accurate to account for changes in absorption spectra when N is added to the sample. We estimated the change of the exciton binding energy before and after doping by using a hydrogen-like model and we found it is of the order of 0.05 eV (see Methods for details). The spectra were averaged over three lattice directions to compare with experimental results obtained from polycrystalline samples. The resulting simulated absorption spectra show that the absorption edge of N-doped BiVO₄ is lower than that of the pristine BiVO₄ by about 0.3 eV (Fig. 4b), confirming that charge-balanced N substitution can indeed enhance visible light absorption at lower energy. This result agrees well with our experimental observation that incorporating ~8% N results in a 0.2 eV reduction of the bandgap.

Our experimental results suggest that in addition to the O vacancies caused by charge-balanced replacement of O²⁻ with N³⁻, additional oxygen vacancies are present serving as electron donors in N₂-treated BiVO₄. Therefore, we performed calculations of N-doped BiVO₄ with excess O vacancies (6% N and 6% O vacancy) (Fig. 5; Supplementary Fig. 10), where half of the O vacancies balance the charges of substitutional N atoms, and the other half provide extra electrons to form polarons. We observed both a reduction of the bandgap by 0.3 eV (Fig. 5a), compared with that of pristine BiVO₄, and the formation of small polarons localized on V atoms (Fig. 5b).

We also note that N-doping increases the mobility of small polarons by changing the static dielectric constant of BiVO₄ (ref. 45). Our computation shows that small polarons’ activation energy of N-doped BiVO₄ (6% N substitution and 3% O vacancies) is lowered by 1.1% and, as a result, the electron mobility is increased by 25% according to the small polaron model (see the Methods section for the computation details). This means that the measured, enhanced \( \phi_{\text{xc}} \) of the N₂-treated sample is not only due to an increase in carrier density but also due to an increase in carrier mobility. To confirm this, we prepared H₂-treated BiVO₄ that has the same O vacancy concentration and, therefore, the same carrier density as the N₂-treated sample but no N incorporation (Supplementary Fig. 11). By comparing electron transport properties of the two samples using APCEs and photocurrents generated by front-side and back-side illuminations (Supplementary Figs 11 and 12), we observed that the electron transport of N₂-treated samples is more enhanced than that of H₂-treated samples. This result suggests that other than the carrier density increase by O vacancies that are common for H₂-treated and N₂-treated samples, the N₂-treated samples have an additional factor improving electron transport. This agrees well with the result from the polaron activation energy calculation that N incorporation results in an increase in polaron mobility.

Altogether, our experimental and computational results show that the simple and mild N₂ treatment used in this study simultaneously enhanced photon absorption, carrier density and carrier mobility, all of which are critical for improving the photovoltaic properties of BiVO₄.

Photo-oxidation of water. The ability of N₂-treated BiVO₄ electrode to photoelectrolyze water was examined in a 0.5 M phosphate buffer (pH 7.2) after oxygen evolution catalysts (OECs), FeOOH and NiOOH, were photodeposited on the N₂-treated BiVO₄ surface sequentially; a FeOOH layer was first photodeposited on the N₂-treated BiVO₄ surface followed by the deposition of a NiOOH (see Methods for the synthesis details). It was reported that the BiVO₄/FeOOH interface minimizes electron–hole recombination at the BiVO₄/FeOOH junction and the NiOOH/electrolyte surface makes the surface charge more favourable while concurrently improving the water oxidation kinetics. As a result, the dual catalyst layer structure provided the best performance compared with single layer or the OEC layers with the reversed order.

Figure 4 | Comparison of pristine and charge-balanced N-doped BiVO₄. (a) Band structures and (b) simulated absorption spectra (imaginary part of dielectric function) of pristine BiVO₄ (black) and BiVO₄ with charge-balanced N-doping (9% O replaced with 6% N and 3% O vacancy) (green). An artificial broadening 0.08 eV is applied to take into account the finite temperature and phonon effects. The highest occupied level at 0 K of BiVO₄ with charge-balanced N-doping was taken as the Fermi level \( E_{\text{Fermi}} \).
Supplementary Fig. 10. Fermi level at the Faradaic efficiency for O2 evolution at 0.6 V versus RHE was 96% attained by a single oxide photon absorber to date (Fig. 6c). The 2.2%, was achieved at 0.58 V, which is the record-high ABPE N-doped BiVO4 with excess O vacancies (6% N and 6% O vacancy) with spin up (red) and spin down (green) configurations. The highest occupied level N2-treated BiVO4/FeOOH interface may no longer be ideal.

BiVO4 combined with the same OECs for water oxidation11, the oxidation and the previously reported photostability of undoped BiVO4 could be increased by the simple N2 treatment. The photocurrent density for water oxidation at 0.6 V versus RHE from 2.71 to 3.47 mA cm–2 (Fig. 6a). The curve was also measured using a two-electrode cell to calculate ABPE (Fig. 6b). The highest ABPE, 2.2%, was achieved at 0.58 V, which is the record-high ABPE attained by a single oxide photon absorber to date (Fig. 6c). The Faradaic efficiency for O2 evolution at 0.6 V versus RHE was 96% (Fig. 6d). The ratio of H2:O2 produced was 1.81:1 (Fig. 6d). Considering that there are no competing reactions available at the cathode, the slight deviation from the stoichiometric H2:O2 production is due to the leak of H2 during manual sampling of H2 for gas chromatography analysis.

The long-term stability of N2-treated BiVO4/FeOOH/NiOOH for water oxidation was examined by measuring J–t plots at 0.6 V versus RHE and was compared with the long-term stability of N2-treated BiVO4 for sulfite oxidation at the same potential (Fig. 6e). The photocurrent for sulfite oxidation was stable for 50 h and no sign of decay was observed, suggesting the presence of nitrogen and oxygen vacancies in the lattice are stable under illumination and electrical bias. The photocurrent for water oxidation was stable for 30 h but after 30 h it gradually decreased. Considering the photostability of N2-treated BiVO4 for sulfite oxidation and the previously reported photostability of undoped BiVO4 combined with the same OECs for water oxidation11, the instability observed during photo-oxidation of water is most likely due to the instability of the N2-treated BiVO4/OEC junction resulting in the loss of OECs over time, which was confirmed by XPS studies (Supplementary Fig. 13). These results suggest that while N2-treated BiVO4 itself is compositionally stable, it will require new OECs to form a more stable N2-treated BiVO4/OEC interface to achieve a long-term stability for photo-oxidation of water.

**Discussion**

Annealing of nanoporous BiVO4 at 350 °C under N2 flow resulted in substitutional incorporation of nitrogen and the formation of O vacancies, which simultaneously enhanced photon absorption, carrier density and carrier mobility. The effect of N incorporation and O vacancies in the BiVO4 lattice were thoroughly examined experimentally and computationally to provide new understanding of the electronic band structures and photoelectrochemical properties of BiVO4. Charge-balanced N-doping (that is, 9% O replaced with 6% N and 3% O vacancy) reduced the bandgap of BiVO4 by elevating the VBM without introducing mid-gap states in the bandgap region. N-doping also decreased the static dielectric constant of BiVO4 and improved the mobility of electrons, which are small polarons. In addition to the O vacancies required for charge-balanced N-doping, the N2-treated BiVO4 contained additional oxygen vacancies, which served as electron donors in N2-treated BiVO4. As a result, the major carrier density as well as the major carrier mobility of BiVO4 could be increased by the simple N2 treatment. The experimental and theoretical studies reported herein may serve as guidelines to further improve photon absorption and charge transport of BiVO4-based photoanodes for more practical and efficient solar water splitting. For example, predicting and incorporating a dopant that can simultaneously improve photon absorption and charge transport may serve as an effective strategy to improve photoelectrochemical performance. Future studies should also include identifying OECs that can optimally interface with BiVO4 electrodes with modified compositions.

**Methods**

**Nitrogen incorporation into BiVO4.** The nanoporous BiVO4 electrode used in this study was prepared using the same method reported in our recent paper11,49. Nitrogen incorporation was achieved by annealing the BiVO4 electrodes at 350 °C for 2 h in a tube furnace while flowing N2. This annealing condition was identified as optimal to generate samples with the best photoelectrochemical properties after trying various annealing temperatures (300–450 °C, ramping rate = 5 °C min–1) and annealing times (1–3 h). The N incorporation shown in this study is the maximum N incorporation that can be achieved by N2 treatment. Increasing temperature or duration of N2 treatment did not increase the N incorporation. When the duration of N2 treatment is shortened, the amount of N incorporated could be reduced but the photocurrent enhancement was also reduced. For example, when the annealing time at 350 °C while flowing N2 was reduced from 2 h to 30 min, the N content, x, in BiVO4–1.5xN was reduced from 0.33 to 0.10 judging from the XPS results and the photocurrent density at 0.6 V versus RHE was reduced from 4.2 to 3.4 mA cm–2.

**Photodeposition of FeOOH/NiOOH OECs on N2-treated BiVO4 electrodes.** The photodeposition of dual-layer oxygen evolution reaction catalysts (that is, FeOOH and NiOOH) on the surface of the N2-treated BiVO4 photoanode were performed using the method described in our recent paper11 with a few modifications. Before photodeposition, the N2-treated BiVO4 was first immersed in 1 M NaOH solution for ~1–2 min to ensure the wetting of its hydrophobic surface. After rinsing the surface with DI water, the photodeposition of FeOOH was carried out.
Photodeposition of NiOOH was carried out on the N₂-treated BiVO₄/FeOOH electrodes using a 0.1 M NaSO₃ solution with pH adjusted to 6.3–7.0 by adding NaOH. To facilitate photodeposition, an external bias of ca. 0.12–0.16 V versus Ag/AgCl (4 M KCl), which was the open circuit potential of the N₂-treated BiVO₄/FeOOH electrodes in the solution in dark, was applied. The optimum deposition time was ca. 25 min (passing a total charge of 20–22 mC cm⁻²). After photodeposition of NiOOH, NiOOH was also electrochemically deposited by applying +1.2 V versus Ag/AgCl (4 M KCl) for 1 min. This was to deposit NiOOH on any bare BiVO₄ or FTO surfaces exposed to the electrolyte. After deposition, the electrodes were washed with DI water and dried at room temperature. The molar ratio of Fe/Ni in optimized N₂-treated BiVO₄/FeOOH/NiOOH electrodes was estimated to be 4.92±0.87 by energy-dispersive spectroscopy (using three samples at the 95% confidence level).

Characterization. The purity and crystal structure of the synthesized electrodes, pristine BiVO₄ and N₂-treated BiVO₄, were examined by X-ray diffraction (Bruker D8 Advanced PXRD, λ = 1.5418 Å, 2θNi, filtered Cu Kα radiation). The crystal morphologies of the electrodes were examined with scanning electron microscopy using a LEO 1530 microscope at an accelerating voltage of 5 kV. The chemical composition of Bi/V in the BiVO₄ electrodes was confirmed to be 0.58±0.02 by a Hitachi S3400-N microscope equipped with an energy-dispersive X-ray spectrometer (Thermo Fisher Scientific Inc.). For the quantitative analysis of the amount of nitrogen doping in N₂-treated BiVO₄, EPM employing a CAMECA SX 50 apparatus was conducted. In sample preparation, the anode material on the FTO film was scraped off and placed on a carbon tape. A precisely quantitative analysis of nitrogen was achieved by calibration using a high-purity GaN as a standard reference. Ultraviolet–visible absorption spectra were obtained on a Cary 5000 UV–vis spectrophotometer (Agilent), in which the sample electrode was fixed in the centre of an integrating sphere to measure all light reflected and transmitted to accurately assess the absorbance. FTO glass was used as the reference for these absorption measurements. XPS spectra were recorded using a K–Alpha X-ray photoelectron spectrometer (Thermo Scientific Inc.) equipped with a monochromated Al Kα line as the X-ray source. The binding energies were calibrated with respect to the residual C (1s) peak at 284.6 eV. Raman spectra of the pristine BiVO₄ and the N₂-treated BiVO₄ electrodes were acquired at room temperature using a Raman spectrometer (Thermo Scientific DXR smart Raman spectrometer). A red laser (780 nm) was used as excitation source. The electrodes were placed such that the BiVO₄ and the N₂-treated BiVO₄ side of electrodes faced the laser source. Capacitance measurements for Mott–Schottky plots were obtained using a SP-200 potentiostat/EIS (BioLogic Science Instrument) with an EC-Lab software package. A sinusoidal modulation of 10 mV was applied at frequencies of 0.5 and 1 kHz. The three-electrode setup was used in a 0.5 M phosphate buffer solution (pH 7.2). All electrodes were masked with epoxy resin to expose the same geometrical area (ca. 0.1 cm²) for this measurement. The zeta potential of pristine BiVO₄ and N₂-treated BiVO₄ were conducted using a zeta potential analyser (Microemetics NanoPlus-2), which measures electro‐phoretic mobilities of charged particles to calculate zeta potentials. This was to compare Helmholtz layer potential drop (Vₜ) of the pristine and N₂-treated BiVO₄ electrodes (equation 1), which is another factor that affects the position of flatband potential (Eₜ) (equation 2). 35

\[
\begin{align*}
E_{\text{t}} & = 0.059 (pH_{\text{PZC}} + pH) \\
E_{\text{t}} & = (\text{NH}_4^+) = \text{V}_{\text{t}} - 4.5
\end{align*}
\]

The point of zero zeta potential (pHₜ) of BiVO₄ and N₂-treated BiVO₄ could not be directly measured because BiVO₄ is not chemically stable near its pHₜ. However, zeta potentials at pH 7.2 solution could still be used to qualitatively compare the pHₜ of BiVO₄ and N₂-treated BiVO₄ and their effects on Eₜ. For the zeta potential measurement, BiVO₄ and N₂-treated BiVO₄ nanoparticles were scratched off the electrode substrates and dispersed in 0.5 M phosphate buffer solution (pH 7.2) using sonication.

Photoelectrochemical measurements. Photoelectrochemical performances of photoanodes prepared in this work were evaluated in a standard three-electrode configuration using a SP-200 potentiostat/EIS (BioLogic Science Instrument). The simulated solar illumination was obtained by passing light from a 300 W Xe arc lamp (Oriel Newport) through a water filter (IR filter/neutr al density filters) and an AM 1.5G filter. Illumination through the FTO side (back-side illumination) was used. The beam passed through an optical filter/an AM 1.5G filter. Illumination from the front side (side illumination) was used. The power density of the incident light was calibrated to 100 mW cm⁻² at the surface of the FTO substrate (before the light penetrates FTO) using a research radiometer (International Light, IL 1700) coupled with a thermopile detector (International Light, SED62/H/N/K15) and a NREL certified reference cell (Photo Emission Tech., Inc.). The beam passed through an optical fibre and the active area of the sample exposed to electrolyte is between ca. 0.1–0.2 cm². Photocurrent measurements were performed in a 0.5 M potassium phosphate (KH₂PO₄) buffer solution (pH 7.2) with or without 1 M sodium sulfate (Na₂SO₄) as a hole scavenger. Before measurements, the electrolyte was thoroughly deaerated by purging with nitrogen. Photocurrents were monitored either while sweeping the potential to the positive direction with a scan rate of 10 mV s⁻¹ or while applying a constant bias. The mean values and confidence intervals of
photocurrent density and electron–hole separation yield provided in the text and Supplementary Table 1 were determined using measurements on three different samples at the 95% confidence level. While all measurements were carried out using a Ag/AgCl (4 M KCl) reference electrode, all results in this work were presented against the RHE for ease of comparison with H2 and O2 redox levels and other reports that used electrolytes with different pH conditions. The conversion between potentials versus Ag/AgCl and versus RHE is determined using the equation below.

\[
E_{\text{versus RHE}} = E_{\text{versus Ag/AgCl}} + E_{\text{Ag/AgCl/reference}} + 0.0591 \times \text{pH}
\]

(4)

IPCE at each wavelength was determined using illumination from a 300 W Xe arc lamp (Oriel Newport) passed through an AM 1.5 G filter, neutral density filters, and an optical filter to approximate the output of the NREL (National Renewable Energy Laboratory) reference solar simulator produced using an Oriel Cornerstone 130 monochromator with a 10-nm bandpass. The intensity of incident light was measured using a research radiometer (International Light, IL 1700) with a calibrated silicon photodiode detector (International Light, SED033). IPCE was measured in 0.5 M phosphate buffer (pH 7.2) with the same three-electrode setup described above for photocurrent measurements, using a Princeton Applied Research Potentiostat/Galvanostat model 263A to apply 0.6 V versus RHE. APCE was obtained by dividing the IPCE by the light harvesting efficiency at each wavelength using the following equations (equations 4 and 5).

\[
\text{APCE}(\%) = \frac{\text{IPCE}(\%) \times \text{LHE}}{100}
\]

(5)

To calculate I_{\text{abs}} (maximum photocurrent density achievable assuming 100% IPCE for photons with energy \(E_g\) of BiVO4 and N2-treated BiVO4, the National Renewable Energy Laboratory (NREL) reference solar spectral irradiance at AM 1.5G (radiation energy (W m\(^{-2}\)) versus wavelength (nm)) was first converted to the solar energy spectrum in terms of number of photons (s\(^{-1}\) m\(^{-2}\) nm\(^{-1}\)) versus wavelength (nm)\(^{50}\). Then, the number of photons above the bandgap energy of each sample shown in this study was calculated using a trapezoidal integration (in 10 nm increments) of the spectrum and was converted to the current density (mA cm\(^{-2}\)). I_{\text{abs}} for pristine BiVO4 and N2-treated BiVO4 were 6.47 and 9.12 mA cm\(^{-2}\), respectively.

Small polaron density and electron–hole separation yield provided in the text and Supplementary Table 1 were determined using measurements on three different samples at the 95% confidence level. While all measurements were carried out using a Ag/AgCl (4 M KCl) reference electrode, all results in this work were presented against the RHE for ease of comparison with H2 and O2 redox levels and other reports that used electrolytes with different pH conditions. The conversion between potentials versus Ag/AgCl and versus RHE is determined using the equation below.

\[
E_{\text{versus RHE}} = E_{\text{versus Ag/AgCl}} + E_{\text{Ag/AgCl/reference}} + 0.0591 \times \text{pH}
\]

(3)

O2 leak rate of the cell. The amount of O2 detected was divided by the amount of O2 expected calculated from photocurrent assuming 100% Faradaic efficiency to O2 evolution was run for 3 h after a 15-min waiting period at open circuit. The O2 leak rate of the cell. The amount of O2 detected was divided by the amount of O2 expected calculated from photocurrent assuming 100% Faradaic efficiency to O2 evolution was run for 3 h after a 15-min waiting period at open circuit. The O2 leak rate of the cell. The amount of O2 detected was divided by the amount of O2 expected calculated from photocurrent assuming 100% Faradaic efficiency to O2 evolution was run for 3 h after a 15-min waiting period at open circuit. The O2 leak rate of the cell. The amount of O2 detected was divided by the amount of O2 expected calculated from photocurrent assuming 100% Faradaic efficiency to O2 evolution was run for 3 h after a 15-min waiting period at open circuit. The O2 leak rate of the cell. The amount of O2 detected was divided by the amount of O2 expected calculated from photocurrent assuming 100% Faradaic efficiency to O2 evolution was run for 3 h after a 15-min waiting period at open circuit. The O2 leak rate of the cell. The amount of O2 detected was divided by the amount of O2 expected calculated from photocurrent assuming 100% Faradaic efficiency to O2 evolution was run for 3 h after a 15-min waiting period at open circuit. The O2 leak rate of the cell. The amount of O2 detected was divided by the amount of O2 expected calculated from photocurrent assuming 100% Faradaic efficiency.
We believe that the formation of small polarons at V sites (1997)(Erratum). To approximate the complex formation energy, we used a super cell with two N dopants and one extra O vacancy. We found that the total energy is lowered by 0.26 eV when forming a N dopant–O vacancy complex, which means that the complex defect is thermodynamically preferred; however, the formation of this complex may be kinetically limited, as the N dopant or O vacancy have to migrate towards each other to form the complex. We note that the band structure of the sample where the N dopant–O vacancy complex is present is more dispersive than that where the N dopants and O vacancies are far apart and the bandgap is 0.2 eV higher.

DFT calculations for charge-balanced N-doped BiVO₄. Projected density of states of BiVO₄ with charge-balanced N-doping (9% O replaced with 6% N and 3% O vacancy) obtained within DFT-PBE + U is shown below (Supplementary Fig. 9). In this case, due to the relative proportion of substitutional N atoms and O vacancies, electrons from O vacancies compensate for extra holes generated by N substitution, balancing the charge. For the charge-balanced N-doping, we have also carried out calculations to study the stability of an N dopant and O vacancy complex, by comparing the total energy of a configuration where the O vacancy is far away from an N dopant (at a ~7–10 Å distance) to that of a configuration where the O vacancy is close to a N dopant (at a ~2 Å distance) in which case N dopants and O vacancies interact strongly to form a complex; we used a supercell with two N dopants and one extra O vacancy. We found that the total energy is lowered by 0.26 eV when forming a N dopant–O vacancy complex, which means that the complex defect is thermodynamically preferred; however, the formation of this complex may be kinetically limited, as the N dopant or O vacancy have to migrate towards each other to form the complex. We note that the band structure of the sample where the N dopant–O vacancy complex is present is more dispersive than that where the N dopants and O vacancies are far apart and the bandgap is 0.2 eV higher.

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Author contributions
K.-S.C. and G.A.G. supervised the project. T.W.K. planned and performed all experiments. T.W.K. and K.-S.C. interpreted the experimental results. Y.P. planned and performed all calculations. Y.P. and G.A.G. interpreted the calculations and consulted with K.-S.C. and T.W.K. to relate the calculation and experimental results. All authors contributed to writing the manuscript.

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