Hetero-type dual photoanodes for unbiased solar water splitting with extended light harvesting

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Metal oxide semiconductors are promising photoelectrode materials for solar water splitting due to their robustness in aqueous solutions and low cost. Yet, their solar-to-hydrogen conversion efficiencies are still not high enough for practical applications. Here we present a strategy to enhance the efficiency of metal oxides, hetero-type dual photoelectrodes, in which two photoanodes of different bandgaps are connected in parallel for extended light harvesting. Thus, a photoelectrochemical device made of modified BiVO4 and α-Fe2O3 as dual photoanodes utilizes visible light up to 610 nm for water splitting, and shows stable photocurrents of 7.0 ± 0.2 mA cm⁻² at 1.23 V_RHE under 1 sun irradiation. A tandem cell composed with the dual photoanodes-silicon solar cell demonstrates unbiased water splitting efficiency of 7.7%. These results and concept represent a significant step forward en route to the goal of >10% efficiency required for practical solar hydrogen production.
The first requirement for efficient conversion of photons to electrons using a semiconductor is its proper bandgap \( E_g \). Photons with energy smaller than \( E_g \) pass through the semiconductor without being absorbed (non-absorption loss), while photons with energy in excess of \( E_g \) lose a part of their energy by emitting phonons (that is, lattice vibrations and heat) on absorption (thermalization losses)\(^1\). These two fundamental losses could be minimized by a multi-junction approach as proven in photovoltaics. Thus, a large \( E_g \) semiconductor absorbs first the high-energy photons of the solar spectrum, and a small \( E_g \) semiconductor placed behind it utilizes the low-energy photons that transmit through the first absorber. As a result, the theoretical efficiency of a multi-junction solar cell can reach 68%, breaking the Shockley–Queisser limit of 31% for a single junction solar cell\(^2\).

We attempt to apply this concept to solar water splitting by combining two well-established metal oxide photoanodes, BiVO\(_4\) and Fe\(_2\)O\(_3\). Virtues of these metal oxide semiconductors are good stability in aqueous solutions\(^3\)-\(^6\), low-cost and easy solution-based processing\(^7\). However, BiVO\(_4\) could use only photons of \( \lambda < 510 \text{ nm} \) due to its rather large \( E_g \) (direct \( \sim 2.6 \text{ eV} \)) and indirect \( \sim 2.4 \text{ eV} \)\(^8\)-\(^14\). In contrast, Fe\(_2\)O\(_3\) has a nearly ideal \( E_g \) of \( \sim 2.0 \text{ eV} \), and can utilize the longer-wavelength (\( < 620 \text{ nm} \)) photons. Yet, its solar-to-hydrogen conversion efficiencies (\( \eta_{\text{STH}} \)) of photoelectrochemical (PEC) water splitting remains modest because of its notoriously poor electrical properties\(^15\)-\(^18\). Hence, by combining these two semiconductors, different parts of the solar spectrum could be utilized. The common way to utilize different \( E_g \)'s for efficient light harvesting is to form a heterojunction\(^12,19,20\). Unfortunately, when BiVO\(_4\) and Fe\(_2\)O\(_3\) are combined to form a bilayer-type heterojunction, this composite photoanode shows an inferior PEC water oxidation performance relative to either of the single-component photoanodes as demonstrated in Supplementary Fig. 1. The ineffective BiVO\(_4\)/Fe\(_2\)O\(_3\) heterojunction originates from their straddling (type I) band alignment instead of a desired staggering (type II) type, which prevents the holes generated in Fe\(_2\)O\(_3\) from transferring to BiVO\(_4\), and thus is not suitable for effective charge separation.

To enhance the light harvesting in two semiconductors of different \( E_g \)'s, here we introduce a concept of 'hetero-type dual photoelectrode (HDP)’ containing two independent liquid–semiconductor junctions as presented in Fig. 1. By using the large \( E_g \) semiconductor as the top absorber and the small \( E_g \) semiconductor at the bottom, both thermalization and non-absorption losses could be minimized. The advantage of our HDP concept is that current-matching of the two electrodes is not required unlike multi-junction solar cells\(^9\) and heterojunction photoelectrodes. Thus, we can independently optimize each photoelectrode, and the performance of the HDP device becomes the simple sum of the individual performance of the two. As a result, the spectral range of light harvesting in the solar spectrum utilized for PEC water splitting is extended.

We note that the HDP concept is analogous to a natural photosynthesis by seaweeds (or marine algae). They develop varying colours depending on the depth of the sea that they inhabit due to the availability of different photons at different depths in the sea—red light can reach only shallow depths because of its low photon energy \( (\lambda > 600 \text{ nm}) \) while blue light \( (\lambda < 420 \text{ nm}) \) can penetrate deeper. Adapting to the availability of photons of varying wavelengths, the seaweed colony is capable of selective light utilization for photosynthesis by varying their habitat depth from green (Chlorophyta), yellow (Phaeophyceae) and then to red (Rhodophyta) as one goes deeper into the sea\(^21\). Instead of developing an ‘ideal’ single-light absorber that can handle all range of photons, the seaweeds develop smart ‘wavelength-optimized’ light absorbers for sequential light harvesting. Such resemblance is rather interesting as the other commonly used light utilization scheme—so called tandem cell also resembles PSI/PSI of natural photosynthesis in using multiple light absorbers.

Here we implement the concept of the HDP using BiVO\(_4\) as the front and \( \alpha \)-Fe\(_2\)O\(_3\) as the back photoanodes for PEC water splitting. To extract the best possible performance of the single photoanodes, we need bulk and surface modifications by doping and co-catalyst, respectively, to improve the charge separation/transfer properties of these semiconductors. As a result, a PEC device made of modified BiVO\(_4\) and \( \alpha \)-Fe\(_2\)O\(_3\) as dual photoanodes shows stable photocurrents of \( 7.0 \pm 0.2 \text{ mA cm}^{-2} \) at 1.23 \( \text{V}_{\text{RHE}} \) under 1 sun irradiation utilizing visible light up to 610 nm. A tandem cell composed of HDP–silicon solar cell demonstrates unbiased water splitting efficiency of 7.7%.

**Results**

Fabrication of photoanodes and their PEC properties. The base BiVO\(_4\) electrode was fabricated by a metal-organic deposition method. Then, 1 at% (optimized) Mo doping and partial reduction treatment were performed to increase mainly the bulk charge separation efficiency as reported in our recent work\(^8\). The reduction treatment via a borohydride decomposition method induced \( V_{\text{OR}} \) defects that effectively increase the charge carrier density in BiVO\(_4\) lattice. Hence, the partial reduction and extrinsic Mo doping treatments synergistically improve the \( n \)-type conductivity of BiVO\(_4\). The other photoanode, haematite Fe\(_2\)O\(_3\), was synthesized by a nitrate decomposition method. This photoanode was doped with 0.5 at% (optimized) Ti, and also partially reduced by the borohydride decomposition. As shown by scanning electron microscopy (SEM) images in Supplementary Figs 2 and 3, BiVO\(_4\) and Fe\(_2\)O\(_3\) have nanoporous, well-connected and non-isotropic morphologies with typical feature sizes of \( \sim 50 \) and \( \sim 10 \text{ nm} \), respectively. Finally, co-catalysts of NiOOH/FeOOH and Ni\(_2\)FeO\(_4\), with a thin TiO\(_2\) overlayer were deposited on the surface of BiVO\(_4\) and haematite, respectively, to improve the charge carrier injection efficiency to the electrolyte. The SEM images in Supplementary Figs 2 and 3 show that the co-catalyst nanoparticles are well dispersed on each semiconductor surface. The X-ray diffraction crystal structures of the photoanode films are standard monoclinic BiVO\(_4\) and haematite \( \alpha \)-Fe\(_2\)O\(_3\) as shown in Supplementary Fig. 4. The X-ray photoemission spectroscopy (XPS) spectra in Supplementary Fig. 5 show binding energies at typically expected positions for BiVO\(_4\) and Fe\(_2\)O\(_3\). See the Methods section and Supplementary Discussion for detailed procedures and discussion for synthesis, optimization and characterization of the two modified photoanodes.
The bulk-modified films were tested first as photoanodes for PEC oxidation of a sacrificial sulphite (SO$_3^{2-}$) solution in a standard three-electrode PEC cell to evaluate their light absorption capability and bulk charge separation efficiency ($\eta_{\text{bulk}}$). As shown in Supplementary Fig. 6, doping with Mo (or Ti) combined with reduction treatment greatly increases the photocurrent and $\eta_{\text{bulk}}$. For BiVO$_4$, reduced 1% Mo:BiVO$_4$ shows $\eta_{\text{bulk}} \sim 90\%$ at 1.23 V$_{\text{RHE}}$, which is comparable to the reported state-of-the-art BiVO$_4$ photoanodes$^{6,8,22}$. Doping and partial reduction treatments are also found to reduce the photocurrent gap between front and back illumination, indicating improved bulk electron transport$^{4,23}$. The same tendency was also observed for Fe$_2$O$_3$, although the highest $\eta_{\text{bulk}}$ was only 41% at 1.23 V$_{\text{RHE}}$. The incident photon to current efficiency (IPCE) values of bare haematite above 400 nm in Supplementary Fig. 7 are relatively low as they originate from an inefficient indirect $d-d$ transition of Fe$^{3+}$ (ref. 18). But the Ti doping and reduction treatments are especially effective in increasing the IPCE of the indirect transition near the absorption edge. As demonstrated by the Mott–Schottky (MS) plots in Supplementary Fig. 8, the main effect of the doping and reduction treatments is to increase the charge carrier density of BiVO$_4$ and Fe$_2$O$_3$, and thereby to improve their bulk charge transfer properties.

Using these two optimized photoanodes, a HDP denoted as BiVO$_4$||Fe$_2$O$_3$ was fabricated by placing the haematite electrode (H, TiO$_2$/0.5% Ti$_2$O$_3$) behind the BiVO$_4$ electrode (H, 1% Mo:BiVO$_4$) in parallel connection as depicted in Figs 1 and 2a. As shown in Fig. 2b, the fabricated BiVO$_4$, Fe$_2$O$_3$ and BiVO$_4$||Fe$_2$O$_3$ electrodes are all highly transparent with a transmittance of 75% at 550 nm for BiVO$_4$, 70% at 650 nm for haematite and 50% at 650 nm for the HDP (Fig. 2f and Supplementary Fig. 9). Hence, ~50% of the incident light remains available for the third absorber (double c-Si) placed behind the HDP, which is needed to generate sufficient bias photovoltage to split water spontaneously as described below.

The PEC performance of the photoanodes (without co-catalysts) was investigated first in a three-electrode configuration (with Pt counter electrode) under AM1.5 illumination. An aqueous solution containing a sacrificial agent (0.5 KPi + 0.5 M Na$_2$SO$_3$) was used as an electrolyte. Since the photo-oxidation of sulphite is so facile, the hole injection efficiency ($\eta_{\text{surface}}$) is essentially 100%. Hence, we can compare bulk photoactivities of the photoanodes by these measurements while avoiding any complications of the hole injection at the semiconductor–electrolyte interfaces. As shown in Fig. 2c, photocurrents of 5.0 ± 0.2, 4.5 ± 0.2, 2.2 ± 0.1 and 7.1 ± 0.2 mA cm$^{-2}$ at 1.23 V$_{\text{RHE}}$ were obtained for BiVO$_4$, Fe$_2$O$_3$, Fe$_2$O$_3$ behind BiVO$_4$ (with no BiVO$_4$ contribution), and BiVO$_4$||Fe$_2$O$_3$, respectively. These photocurrents are optimized values by adjusting the thickness of BiVO$_4$ and Fe$_2$O$_3$, which can be easily regulated by changing the quantity of precursor solution. (See Fig. 2d, Supplementary Figs 10 and 11 and Methods part for details).

Overall, the HDP shows an increased photocurrent by ~29.3% from that of a single BiVO$_4$ photoanode. Its photocurrent is almost the same as the sum of photocurrents generated by BiVO$_4$ and Fe$_2$O$_3$ behind BiVO$_4$, indicating that the HDP concept is indeed operating. It is also noteworthy that the onset potential of the BiVO$_4$||Fe$_2$O$_3$ combination is ~0.2 V$_{\text{RHE}}$, which is the same as that of BiVO$_4$ alone and far lower than that of a single haematite photoanode (~0.4 V$_{\text{RHE}}$).

The IPCE of BiVO$_4$ in Fig. 2e is significantly higher than that of haematite in the range of 300–450 nm, justifying BiVO$_4$ as the first absorber. The IPCE of the HDP further increases up to ~95% in this region due to the additional photocurrent generated from haematite using the transmitted light through the BiVO$_4$ electrode. In the range of 450–510 nm, IPCE of BiVO$_4$ drops sharply due to the reduced light-harvesting efficiency close to its absorption threshold and indirect band transition (direct: ~2.6 eV; indirect: ~2.4 eV)$.^{14}$ This is an important reason why the theoretical maximum photocurrent (7.5 mA cm$^{-2}$) of BiVO$_4$ is very difficult to achieve with a single BiVO$_4$ absorber. However, haematite can utilize the transmitted light in this region efficiently as an additional absorber. In the region of 510–610 nm, only haematite contributes to the overall performance of HDP. Even though the IPCE values in this region drop below 20%, the effect is very significant since more than 50% of the solar energy exploitable by a photoelectrode lies in this region. The theoretical maximum photocurrent of Fe$_2$O$_3$ is ~13.6 mA cm$^{-2}$, and nearly a half of it comes from photons with 500–620 nm range$.^{4}$ Thus, this region has to be exploited to further improve the performance of HDP.

**PEC water splitting with an external bias.** The performance of the photoanodes is now studied for water oxidation under 1 sun illumination in a three-electrode PEC cell without any sacrificial agent. When used as a single photoanode, electrolytes of pH 7 and >12 are optimal for BiVO$_4$ and Fe$_2$O$_3$, respectively, for their high activity and stability. Hence, the first important task to apply the HDP for PEC water splitting is to find an optimum electrolyte suitable for both BiVO$_4$ and Fe$_2$O$_3$. In a screening test summarized in Supplementary Figs 12 and 14, we found that pH 9.2 (1.0 M bicarbonate KCl solution) was a good compromise for the two semiconductors and selected co-catalysts. Next step is to find the best co-catalysts to promote the PEC water oxidation activity and stability by accelerating the hole injection to the electrolyte to avoid surface charge recombination, and to protect the semiconductor from photochemical corrosion. Thus, the co-catalyst selection process shown in Supplementary Figs 12–14 and described in the Supplementary Information yielded NiOOH/FeOOH for BiVO$_4$ and Ni$_2$FeO$_4$/TiO$_2$ for Fe$_2$O$_3$ as the best oxygen evolution co-catalysts. In particular, the thin TiO$_2$ layer deposited on the surface of Fe$_2$O$_3$ passivates the surface states of haematite (Supplementary Fig. 13) that cause undesired electron–hole recombination and potential drop within the Helmholtz layer$.^{25}$ Hence, the treatment not only improves photocurrent generation but also brings a negative shift of the onset potential and a greater photovoltage from the electrode.

The water oxidation photocurrents of completed BiVO$_4$, Fe$_2$O$_3$ and Fe$_2$O$_3$ behind BiVO$_4$ photoanodes were 5.0 ± 0.1, 4.0 ± 0.2 and 2.0 ± 0.1 mA cm$^{-2}$ at 1.23 V$_{\text{RHE}}$, respectively. The BiVO$_4$||Fe$_2$O$_3$ HDP photoanode recorded stable photocurrents of 7.0 ± 0.2 and 8.0 ± 0.2 mA cm$^{-2}$ at 1.23 V$_{\text{RHE}}$ and 1.5 V$_{\text{RHE}}$, respectively. This PEC performance represents the highest ever reported for stable metal oxide photoelectrodes to the best of our knowledge. The benchmarking results against other studies are presented in Supplementary Table 1, in which it can be seen that not only HDP but also the individual BiVO$_4$ and Fe$_2$O$_3$ photoanodes are among the top performers within their classes. The performance was highly reproducible as demonstrated in Supplementary Fig. 15 and most of the photocurrents came from water splitting to H$_2$ and O$_2$ gases with almost complete faradaic efficiency (Fig. 3d). The HDP utilized visible light up to 610 nm for water splitting as shown by action spectra in Fig. 3e–g. The photocurrents and IPCEs for water oxidation show similar values to those in Fig. 2 for sacrificial sulphite oxidation, indicating that used co-catalysts are highly effective, with hole injection efficiencies ($\eta_{\text{surface}}$) of 89–100%.

**Unbiased solar water-splitting tandem cell.** Eventually, the developed HDP must be successfully applied to a practical solar water splitting system that operates without external energy supply. Thus, unbiased solar water splitting was demonstrated...
with a tandem cell fabricated by integrating a thin film Si solar cell behind the HDP BiVO₄||Fe₂O₃ photoanode as schematically shown in Fig. 4a. We also fabricated monolithic version of the tandem cell (artificial leaf) that could perform overall water splitting (Fig. 4b, Supplementary Fig. 16 and Supplementary Movies 1 and 2 operating under simulated and actual outdoor sun illumination). The monolithic device possesses simplicity and versatility for small scale or mobile applications. By using a series-connected two parallel (2p) c-Si solar cell with a photovoltage of ~1.2 V as the bottom absorber, this system can be classified as a ‘Q6’ system, that is, quadruple absorbers that need six photons for production of a H₂ molecule. The crossing points of performance curves of photoanodes and the solar cell give the expected operation photocurrents of BiVO₄, Fe₂O₃ and BiVO₄||Fe₂O₃ photoanodes at 4.5, 3.2 and 6.3 mA cm⁻², which correspond to solar-to-hydrogen conversion efficiency (ηSTH) of 5.6%, 3.9% and 7.7% (Fig. 4c, Supplementary Figs 17 and 18), respectively. As shown in Supplementary Fig. 18, the actual tandem cell reproduces these expected values, which represent one of the highest ηSTH obtained from unbiased solar water splitting in a tandem PEC cell using stable metal oxide photoelectrodes (see Supplementary Table 2 and Supplementary Fig. 19 for benchmarking). There was no sign of decay during the continuous run (8 h) of the tandem cell, indicating a complete isolation of the solar cell component from the electrolyte (Fig. 4d). Thus, we present the highest performing HDP photoanode and tandem cell for unbiased solar water-splitting system.

**Discussion**

In summary, we presented a HDP as a new strategy to fabricate a stand-alone, highly efficient solar water-splitting system. With a...
HDP of BiVO₄||Fe₂O₃, we obtained a water oxidation photocurrent density of 7.0 ± 0.2 mA cm⁻² at 1.23 VRHE, which sets a new performance benchmark for metal oxide photoanodes. As summarized in Fig. 5 and Supplementary Table 1, it is the first metal oxide photoanode to break the barrier of 7.0 mA cm⁻² at 1.23 VRHE. It is also meaningful that the result demonstrates how to move forward beyond BiVO₄ photoanode, which is the current forerunner material in solar water-splitting performance but is hampered by its relatively large bandgap. The HDP photoanode was successfully incorporated into a tandem cell with a c-Si solar cell for unbiased solar water splitting to demonstrate a stable and reproducible ZSTH of 7.7%. There are two easily conceivable ways to reach ZSTH higher than 10%, which is required for practical solar water splitting and the goal of most solar fuel research projects in progress worldwide. First, the saturated photocurrent of the current HDP is already over 8.3 mA cm⁻² (Fig. 3a) and thus ηSTH > 10% (8.1 mA cm⁻²) could be obtained by further reducing the onset potential of the photoanode. Second, if the bulk charge separation efficiency of the Fe₂O₃ electrode increases from its current 40% to a modest 50%, a photocurrent of 8.1 mA cm⁻² or ZSTH of 10.1% is expected. Considering the rapid progress made in the last decade as depicted in Fig. 5, it seems highly likely that those two issues can be solved and that the goal of 10% ZSTH can be achieved within the foreseeable future. Hence, the HDP concept proposed here represents a significant step forward en route to practical solar hydrogen production.

Methods
Preparation of BiVO₄ films. All chemicals used in this study were of analytical grade and used without further purification. BiVO₄ film was prepared by a modified metal-organic decomposition method with a slight modification from our previous procedure. Thus, 0.2 M Bi(NO₃)₃·5H₂O (99.8%; Kanto Chemicals)
stabilization of the tandem cell). Photoanodes were NiOOH/FeOOH/H, 1% Mo:BiVO4 and Ni2FeO photoelectrode. (Supplementary Movie 2) and parallel-connected Si solar cells (2c-Si). Thus, 0.5 M Fe(NO3)2 electrolyte of 1.0 M KC1, pH 6. NATURE COMMUNICATIONS | DOI: 10.1038/ncomms13380 | www.nature.com/naturecommunications

Supplementary Table 1. Different from the standard 1.23 VRHE. Numerical data are given in symbols indicate that photocurrent values were measured at a potential 6. NiOOH/FeOOH co-catalyst deposition on the BiVO4 film. The NiOOH/FeOO4 co-catalysts were deposited utilizing photo-assisted electrodeposition (PED) under AM 1.5G illumination. FeOOH was deposited from a 0.1 M Fe2O3 metal oxide film (2 cm × 2.5 cm) was placed and finally the 200 ml alumina crucible was covered with an alumina cover. This reactor was put in a preheated furnace at 500°C for 10 min. Then the crucible was immediately taken out from the furnace and cooled down naturally.

2-methoxymethanol (98.0%; Kanto Chemicals) and acetyl acetone (> 99.0%; Kanto Chemicals). Volume ratio of 2-methoxymethanol and acetyl acetone was 7:3. Then, 500 mg of polyethylene glycol 8000 (polymer mass) (> 99.0%; Sigma Aldrich) was added in 10 ml of precursor solution as a polymer binder. Prepared solution was sonicated for 1 h to achieve a homogeneous but opaque red wine-like coloured solution. Then, a Ti precursor solution was added as dopant with a FeTi atomic ratio of 0.995:0.005 for 0.5% Ti concentration. The Ti precursor was 0.5 M Ti(IV) propoxide (99%; Sigma Aldrich) and 2-methoxymethanol (98.0%; Kanto Chemicals) solution. For the Fe2O3 film formation, 6 μl of the prepared solution were dropped on FTO glass (2 cm × 2.5 cm), and dried in Ar atmosphere for 15 min. After full drying (colour of precursor film became violet), the film was preheated at 80°C for 10 min (the precursor film became brown) in Ar atmosphere and heat-treated at 500°C for 10 min in the furnace. To obtain a desired film, the process was repeated for three times and finally the film was annealed at 500°C for 75 min.

For TiO2 surface treatment, 0.05 M titanium oxy acetylacetonate (98%; Sigma Aldrich) and 2-methoxymethanol (98.0%; Kanto Chemicals) solution was used. The as-prepared Fe2O3 film was coated with a Ti(IV) precursor by spin coating (1,000 r.p.m., 20 s, 2 times) and heat-treated at 500°C for 10 min.

Reduction treatment of metal oxide films. Reduction treatment was conducted using a borohydride decomposition method. First, 16 mmol of NaBH4 (> 98%; Sigma Aldrich) was put in a 200 ml alumina crucible and another smaller alumina bottle (15 ml) was put on the NaBH4 powder. In this smaller bottle, the as-prepared metal oxide film (2 cm × 2.5 cm) was placed and finally the 200 ml alumina crucible was covered with an alumina cover. This reactor was put in a preheated furnace at 500°C for 30 min. Then the crucible was immediately taken out from the furnace and cooled down naturally.

NIIOH/FeOOH co-catalyst deposition on the BiVO4 film. The NiOOH/FeOO4 co-catalysts were deposited utilizing photo-assisted electrodeposition (PED) under AM 1.5G illumination. FeOOH was deposited from a 0.1 M Fe2O3 metal oxide film (2 cm × 2.5 cm) was placed and finally the 200 ml alumina crucible was covered with an alumina cover. This reactor was put in a preheated furnace at 500°C for 30 min. Then the crucible was immediately taken out from the furnace and cooled down naturally.

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NiFeO2 co-catalyst deposition on Fe2O3 film. To deposit Ni3Fe2O5−x NiFeO2, and NiFeO2 co-catalysts on the Fe2O3 film, a single-solution method was used following Peerlings et al.29 A precursor solution containing Ni(NO3)2·3H2O (99.0%; Sigma Aldrich) and Fe(NO3)3·3H2O (99.0%; Kanto Chemicals) was prepared with 2-methoxyethanol (98.0%; Kanto Chemicals) and mixtures of NiFeO2 of proper ratios were made. The mixture of Ni + Fe solutions was diluted to a concentration of 0.01 M before usage. For deposition of the electrolytically grown 1 ml of the mixture solution was dropped on Fe2O3 photoelectrode (0.24 cm²) and dried in air, and the photoelectrode was rinsed with 0.1 M KOH for 10 s.

For electrochemical analysis, above precursors with a thicker concentration (0.2 M) were used for NiO solar cell anode for electron intake. Measurements of PEC performance (200 kV).

Measurements of PEC performance

PEC measurements were carried out using a solar simulator (Oriel 70260, UV–vis monochromator) with a bandwidth limit of 5 nm. The intensity of light was measured before IPCE measurements by photodiode detector (Oriel 70260).

Calculation of IPCE was carried out by the formula

\[ \text{IPCE}(\%) = \frac{\lambda 	imes P}{E_{\text{light}} 	imes 100} \]

where \( \lambda \) = photodcurrent density (mA cm⁻²), \( P = \) light power density (mW cm⁻²) at \( \lambda \), and \( \lambda \) = wavelength of incident light (nm).

The MS plot was used to determine electrochemical properties using the equation:

\[ \frac{1}{C_0^2} = \frac{2(V - V_0 - KT/e)}{\ln(1 + \exp(-eV_0/eV))} \]

where \( C_0 \) = capacitance of photoanode (metal oxide + electrolyte double layer and so on), \( e = \) charge of electron (C), \( V_0 = \) dielectric constant of BiVO4 and FeOO, \( V_0 = \) permittivity of vacuum, \( V = \) applied bias (versus RHE), \( V_0 = \) flat band potential (versus RHE), \( k = \) Boltzmann constant, \( N_0 = \) donor density for n-type semiconductor (cm⁻³), \( A = \) surface area of photoanode and \( T = \) temperature (K).

PEC H2 and O2 evolution measurements. Using Ar as a carrier gas, the amounts of H2 and O2 gases evolved from the PEC cell were analysed using a gas chromatograph (HP5890, molecular sieve 51 column) equipped with a thermal conductivity detector. Light source and electrolyte were the same as those used for above PEC measurements, and the gas products were sampled every 20 min.

Characterization of BiVO4 and 2-Fe2O3 on doping and H2 treatment. The X-ray diffraction crystal structures of the photoanode films were standard monoclinic Bi2O3 and haematite \( \alpha \)-Fe2O3 as shown in Supplementary Fig. 4. In the X-ray spectra of Supplementary Fig. 4, the binding energies of Bi (4f7/2 at 164.3 eV and 4f5/2 at 159.1 eV) and Fe (2p3/2 at 523.5 eV and 2p1/2 at 515.9 eV) correspond to standard BiVO4, \( \sim \)0.3 eV shift to lower binding energies was observed after hydrogen treatment due to the partial reduction of Bi3+ \( \rightarrow \) V2+ as reported previously for metal oxide semiconductors treated with H2 or N2 (refs 8,22). No clear shift is observed for Mo 3d (3d5/2 at 235.9 eV and 3d3/2 at 232.6 eV) showed near absent change due to small XPS signal, Fe 3d also showed a lower energy shift (\( \sim \)0.3 eV) as an indication of reduction. Interestingly, Ti 2p, derived from dopant and surface treatment for Fe2O3 also showed a shift to lower binding energies (\( \sim \)0.4 eV). The binding energy of Ti 2p was lower than that of the other transition metal Ti 2p (2p3/2 at 459.0 eV)23 because it was in a doped state or interaction with Fe2O3.

Effects of the combined doping and hydrogen treatment on the charge carrier density (\( N_0 \)) were studied by MS analysis in Supplementary Fig. 8 in connection to PEC water oxidation performance. Thus, \( N_0 \) (cm⁻³) was calculated assuming that the geometric area (1 cm² in the present case) was the actual surface area of material for all samples according to the equation:

\[ N_0 = \frac{2\epsilon e(D/V)}{d} \]

where \( \epsilon = \) charge of electron (1.6 \times 10⁻¹⁹ C), \( e = \) dielectric constant of BiVO4 (\( \sim \)68), \( \epsilon = \) permittivity of vacuum and \( V = \) applied bias versus RHE8,31,32. In agreement with previous reports, Mo doping for BiVO4, Ti doping for Fe2O3 and H2 treatment for both metal oxides, decreased the slope of 1/C² indicating the increased charge carrier density23,30,31,33. Oxygen vacancies formed by hydrogen treatment introduce excess minority carriers as \( V_0 \) : a more stable n-type dopant in metal oxides23,33,36. The reduced XPS-binding energies for the metallic elements observed for BiVO4 and Fe2O3 (Supplementary Fig. 5) are consistent with the reduced oxidation state one would expect for oxygen deficient metal oxides.

Co-catalyst loading and the characterization. To promote water oxidation further, oxygen-evolving co-catalysts were used. For BiVO4, Co-Pi is known to be one of the most active co-catalyst8,19, but its stability is poor. Hence, NiOOH/FeOOH-modified photoanodes were used here, and our NiOOH/FeOOH/H, 1% MoBiVO4 photoanode showed an photocurrent of 5.0 ± 0.2 mA cm⁻² at 1.23 V vs RHE. This is close to the state of the art, and corresponds to an applied bias photon-to-current efficiency (ABPE) of 2.08% as shown in Supplementary Fig. 9, which is comparable to the highest value recorded for metal oxide photoelectrodes (NiOOH/FeOOH/BiVO4, ABPE of 2.2% (ref. 22)). For Fe2O3, NiOOH/FeOOH showed one of the most active among co-catalysts tested in this work, including Co-Pi, FeOOH, NiOOH, and Fe2O3. In particular, Ni3Fe2O5 was produced by our new synthesis method using the reduction of a nitrate salt solution and in situ activation during PEC operation showed the best results. XPS analysis in Supplementary Fig. 5 indicates that the NiOOH/FeOOH co-catalyst has oxidation states close to Fe3+ and Ni2+/3+ as reported37. The oxidation state of Ni in Ni3Fe2O5 is also likely to be mixed Ni2+/3+ (refs 10,38). The O1s signal for the NiOOH/FeOOH-modified photoanodes shows a pronounced extra peak at 531.3 eV, which confirms that the NiOOH/FeOOH/Fe2O3 co-catalysts are in the oxy hydroxide form29,30.

Surface modification of Fe2O3 and the PEC water-splitting performance. Recombination at surface states is a well-known issue for unmodified Fe2O3 photoanodes (Supplementary Fig. 13). In addition to lowering the photocurrent, these states can also cause Fermi level pinning, which causes part of the potential

\[ \text{IPCE} = \frac{1}{\lambda \times P} \times 100 \]

NiFeO2 co-catalyst deposition on Fe2O3 film. To deposit Ni3Fe2O5−x NiFeO2, and NiFeO2 co-catalysts on the Fe2O3 film, a single-solution method was used following Peerlings et al.29 A precursor solution containing Ni(NO3)2·3H2O (99.0%; Sigma Aldrich) and Fe(NO3)3·3H2O (99.0%; Kanto Chemicals) was prepared with 2-methoxyethanol (98.0%; Kanto Chemicals) and mixtures of NiFeO2 of proper ratios were made. The mixture of Ni + Fe solutions was diluted to a concentration of 0.01 M before usage. For deposition of the electrolytically grown 1 ml of the mixture solution was dropped on Fe2O3 photoelectrode (0.24 cm²) and dried in air, and the photoelectrode was rinsed with 0.1 M KOH for 10 s.

For electrochemical analysis, above precursors with a thicker concentration (0.2 M) were used for NiO solar cell anode for electron intake. Measurements of PEC performance (200 kV).

Measurements of PEC performance

PEC measurements were carried out using a solar simulator (Oriel 70260, UV–vis monochromator) with a bandwidth limit of 5 nm. The intensity of light was measured before IPCE measurements by photodiode detector (Oriel 70260).

Calculation of IPCE was carried out by the formula

\[ \text{IPCE}(\%) = \frac{1}{\lambda \times P} \times 100 \]

where \( \lambda \) = photodcurrent density (mA cm⁻²), \( P = \) light power density (mW cm⁻²) at \( \lambda \), and \( \lambda \) = wavelength of incident light (nm).

The MS plot was used to determine electrochemical properties using the equation:

\[ \frac{1}{C_0^2} = \frac{2(V - V_0 - KT/e)}{\ln(1 + \exp(-eV_0/eV))} \]

where \( C_0 \) = capacitance of photoanode (metal oxide + electrolyte double layer and so on), \( e = \) charge of electron (C), \( V_0 = \) dielectric constant of BiVO4 and FeOO, \( V_0 = \) permittivity of vacuum, \( V = \) applied bias (versus RHE), \( V_0 = \) flat band potential (versus RHE), \( k = \) Boltzmann constant, \( N_0 = \) donor density for n-type semiconductor (cm⁻³), \( A = \) surface area of photoanode and \( T = \) temperature (K).
drop to fall across the Helmholtz layer. This leads to a lower photovoltage ($V_{ph}$) and an undesired positive shift of the photocurrent onset potential$^{30}$. Recently, there have been many successful examples of passivating the surface states of haematite by depositing metal oxide overlayers$^{31-42}$. Here we passivate these surface states by depositing a thin TiO$_2$ layer on the surface of hydrogen-treated 0.5% TiFe$_2$O$_3$ using a facile solution-based method. As shown in Supplementary Fig. 13, this increases the photocurrent density markedly from 0.88 to 3.0 mA at 1.23 V$_{RHE}$ in a 1.0 M NaOH electrolyte and shifted the onset potential cathodically by ~115 mV. There was no obvious change in the carrier density of haematite on TiO$_2$ loading and the flat band potentials are similar, as demonstrated by the MS plots (Supplementary Fig. B1). Thus, our optimized Ni$_2$FeO$_x$-coated, hydrogen-treated and TiO$_2$-modifed 0.5% TiFe$_2$O$_3$ photoanodes showed photocurrents of 3.5–4.1 mA cm$^{-2}$ at 1.23 V$_{RHE}$ in a pH 9.2 KCl electrolyte, which is amongst the highest ever recorded for Fe$_2$O$_3$-based photoanodes in near-neutral electrolytes, and comparable with reported top-performing NiFeO$_x$/FeO$_x$ (ref. 4), NiFeO$_x$/Al$_2$O$_3$/Si:Fe$_2$O$_3$ (ref. 10) photoanodes. Interestingly, loading of the Ni$_2$FeO$_x$-co-catalyst on Fe$_2$O$_3$ photoanode significantly reduced the performance gap between pH 9.2 (1.0 M KCl) and pH 13.6 (1.0 M KOH) (Supplementary Fig. 14). In the meantime, it would be more effective for practical application as water oxidation efficiency (especially Fe$_2$O$_3$) can be maximized if HDP can be operated in highly basic solution, owing to pH gradient problem in mild electrolyte condition$^{33}$.

Data availability. The data that support the findings of this study are available from a corresponding author (I.S.L.) on request.

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