1D Co-Pi Modified BiVO$_4$/ZnO Junction Cascade for Efficient Photoelectrochemical Water Cleavage

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The most important factors dominating solar hydrogen synthesis efficiency include light absorption, charge separation and transport, and surface chemical reactions (charge utilization). In order to tackle these factors, an ordered 1D junction cascade photodeode for water splitting, grown via a simple low-cost solution-based process and consisting of nanoparticulate BiVO$_4$ on 1D ZnO rods with cobalt phosphate (Co-Pi) on the surface is synthesized. Flat-band measurements reveal the feasibility of charge transfer from BiVO$_4$ to ZnO, supported by PL measurements and photocurrent observation in the presence of an efficient hole scavenger, which demonstrate that quenching of luminescence of BiVO$_4$ and enhanced current are caused by electron transfer from BiVO$_4$ to ZnO. A dramatic cathodic shift in onset potential under both visible and full arc irradiation, coupled with a 12-fold increase in photocurrent (ca. 3 mA cm$^{-2}$) are observed compared to BiVO$_4$, resulting in -47% IPCE at 410 nm (4% for BiVO$_4$) with high solar energy conversion efficiency (0.88%). The reasons for these enhancements stem from enhanced light absorption and trapping, in situ rectifying electron transfer from BiVO$_4$ to ZnO, hole transfer to Co-Pi for water oxidation, and facilitating electron transport along 1D ZnO.

1. Introduction

There has been intense research into the development of visible-light active semiconductor photocatalysts for solar energy conversion, in particular, for oxidation and reduction of water into molecular oxygen and hydrogen, which can be used as a clean, renewable fuel source. There are several challenges that need to be addressed before the implementation of such a process. The semiconductor must possess a suitable band-gap, preferably in the visible range, with a conduction band more negative than 0 V and the valence band more positive than 1.23 V. It is widely accepted that the most important factors dominating solar hydrogen synthesis efficiency include: i) light absorption; ii) charge separation and transport; and iii) surface chemical reactions (charge utilization).[2,3] Numerous materials have been reported to split water under UV and/or visible irradiation via a photoelectrochemical process; the most widely reported being TiO$_2$, SrTiO$_3$, and KTaO$_3$ as well as Fe$_2$O$_3$, WO$_3$, and BiVO$_4$. However the current solar to fuel conversion efficiency is still moderate. A new material strategy therefore is required to enhance the energy conversion efficiency, such as via manipulating the aforementioned important factors. Suppression of charge recombination is one of the key solutions, which can be attempted in a number of ways: i) the use of scavengers (sacrificial solutions), which can remove either holes or electrons in the system so that only one half of the water splitting reaction can be studied in isolation (either reduction or oxidation); ii) variation of the morphology of the photocatalyst, which has been shown to improve photocatalytic activity due to the increase in surface area and the shortening of charge carrier diffusion pathways to the surface; and iii) the most promising way is to create a heterojunction, whereby charge carriers are generated in one photocatalyst and subsequently vectorially transferred to the other material, mimicking natural photosynthesis. Beyond this, the separated charge transport also needs to be enhanced to improve the energy conversion efficiency.

Here, we attempted to design a special morphology of heterojunction to tackle the above-mentioned three dominating factors in order to achieve efficient photoelectrochemical water splitting to molecular H$_2$ and O$_2$. In other words, an ordered 1D morphology will be used to enhance light absorption by light trapping effect,[10,11] a heterojunction is used for in situ rectifying charge transfer and separation as well as the appropriate charge acceptor will be selected to further facilitate the transport of separated charges; finally an efficient co-catalyst is utilized to accelerate the surface reactions, as indicated in Scheme 1 composed of a junction cascade.

Monoclinic BiVO$_4$, as a well-known, stable n-type semiconductor with a direct band-gap of approximately 2.4 eV, was selected as the robust light absorber due to its reported extremely high visible driven photocatalytic activity for oxygen evolution from aqueous AgNO$_3$ solution in a suspension system.[12] There are, however, a number of limiting factors which act to reduce the energy conversion efficiency of the
electron transport due to their internal electric field in other applications.\cite{16} Furthermore, the 1D structure, in theory, can substantially trap photons, which should increase light absorption compared with a flat surface. Finally, addition of an earth abundant cobalt phosphate complex upon the surface of BiVO₄ forms a junction cascade Co-Pi/BiVO₄/ZnO, in which the complex Co-Pi acts as a hole acceptor and catalytic site to speed up water oxidation. This new design strategy, comprised of a bi-junction, represents the first successful example of BiVO₄-based junction cascade photoelectrode for water splitting, and has been fully investigated and the performance optimized in the paper. The stability of the novel structure was also discussed.

2. Results and Discussion

Rare BiVO₄, ZnO and 1D BiVO₄/ZnO heterojunction films were grown directly onto FTO-coated glass substrates using a combination of solution-based hydrolysis-condensation synthesis and spray deposition (see Experimental Section). The X-ray diffraction (XRD) patterns for ZnO, BiVO₄ and BiVO₄/ZnO are displayed in Figure 1a. XRD confirmed the presence of ZnO exhibiting a Wurtzite structure with strong preferred orientation; the growth direction of the nanorods was assigned to the <0002> direction as expected for the nanorod morphology of ZnO grown from acetate seed crystals, which results in c-axis texturing.\cite{27,28} The as-deposited BiVO₄ films grown via spray deposition at 200 °C were of a dark-yellow to brown appearance, and X-ray diffraction analysis revealed no crystalline phase(s) at this temperature (not shown). Subsequent heat treatment in air at 450 °C for 3 h is necessary which yields pure monoclinic BiVO₄ possessing the Scheelite structure. The heterojunction BiVO₄/ZnO films were grown through directly spraying the Bi-V solution onto the ZnO nanorods followed by heat treatment at 450 °C.

The UV-vis absorption spectra of BiVO₄, ZnO nanorods, and BiVO₄/ZnO heterojunction are shown in Figure 1b. The bandgap ($E_g$) of a semiconductor could be inferred from its UV-vis spectra using the following equation:

$$
(αhν)^n = A(hν - E_g)
$$

(1)

where $α$ is the absorption coefficient, $hν$ is the energy of photon, $n$ represents the index which depends on the electronic transition of the semiconductor (for direct band-gap semiconductors BiVO₄ and ZnO, $n = 2$). In addition, $A$ is a proportionality constant related to the material. The band-gap energy was obtained from the intercept of the tangent line in the plot of $(αhν)^2$ versus energy, and the value was determined to be ~2.3 eV for BiVO₄ and ~3.2 eV for ZnO (see Supporting Information Figure S1a). The 1D BiVO₄/ZnO heterojunction displayed much higher absorption within the visible region of the spectrum (Figure 1b), with the edge at ~490 nm corresponding to BiVO₄ and the edge at ~390 nm corresponding to ZnO nanorods. Similar increase caused by light trapping has been observed on bare ZnO nanowires compared to flat ZnO films,\cite{10} as well as on CdTe/ZnO nanowire arrays.\cite{11} On the other hand, formation of mid-gap states caused by, amongst other factors, the defect chemistry of ZnO, could lead to the formation of broad mid-gap states and show an enhanced visible band absorption. However,
the junction shows very similar band-gap absorption (similar profile) to BiVO₄ except enhanced intensity in the visible region. Therefore the obvious enhanced absorption in the visible region (>400 nm) is attributed to the light-trapping effect as expected due to a 1D aligned morphology of the heterojunction. A somewhat red-shift in the spectrum might be due to the formation of shallow levels within the band gap as a result of the presence of impurity atoms in the lattice and/or strong disturbances of local symmetry.[29] The Raman spectrum of the 1D BiVO₄/ZnO heterojunction (Supporting Information Figure S1b) revealed a strong peak at 440 nm, consistent with the high-E₂ vibration of wurtzite ZnO,[30] whilst the other strong peak at ≈823 nm corresponds to the v₁ symmetric stretching mode of monoclinic BiVO₄[31] and provides further evidence of the incorporation of both materials within the same photoanode.

The top-down and side-on SEM image of ZnO nanorods are displayed in Figure 1c. Growth of vertically aligned ordered ZnO nanorods for 4 h via hydrolysis-condensation synthesis results in very homogeneous nanorods with a length of 900 nm and a diameter of 70 nm.[28] Top-down SEM images of bare BiVO₄ after heat treatment reveals a dense morphology of good substrate coverage and uniformity (see Supporting Information Figure S2a). The top-down SEM image of the heterojunction BiVO₄/ZnO film (Figure 1d) reveals that the spray deposition procedure mainly introduced BiVO₄ agglomerations at the tops of the nanorods which can, as expected, facilitate charge separation at the interface of BiVO₄ and ZnO. The side view of the junction confirms that the coating procedure of BiVO₄ did not change the length, nor the ordered morphology of the ZnO substrate (see Supporting Information Figure S2b), which also reveals the major BiVO₄ coating to be on the top surface of the vertically aligned nanorods to form the intimate contact, which is important for the proposed fast charge transfer between them.

Impedance measurements conducted on BiVO₄ and ZnO electrodes in 0.2 M Na₂SO₄ electrolyte in the dark allowed the construction of Mott-Schottky plots from which the flat-band potentials (E_f) of the two materials were measured. Figure 2a shows the Mott–Schottky plots of BiVO₄ and ZnO electrodes measured at 1 kHz. Using our device we observed poor reproducibility at higher frequencies due to the frequency dependence of charge carrier density and mobility, however in all cases the intercepts for E_f were very close in agreement with each other. The E_f of the BiVO₄ electrode was estimated to be −0.53 V (vs Ag/AgCl at pH 6.5) or +0.05 V (vs RHE) and is very similar to the value measured at 1000 Hz by Zou et al, for their undoped BiVO₄ electrodes in 0.5 M Na₂SO₄ (pH 6.5).[32] E_f for ZnO nanorods was estimated as −0.33 V (vs Ag/AgCl at pH 6.5) or +0.25 V (vs RHE). The difference in the E_f values for BiVO₄ and ZnO measured under identical conditions in our laboratory indicate that electron transfer in principal from BiVO₄ to ZnO is feasible as E_f is considered to be located just under the conduction band of n-type semiconductors.[23] Even so, there are many values reported in the literature for the E_f of BiVO₄, which tend to be in the range of −0.7 to −0.3 V vs Ag/AgCl, pH 5.8–7.[22–24] Similarly, for ZnO nanorods, values for E_f have...
been reported in the range of +0.2 V to –0.29 V (vs Ag/AgCl, pH 7.4) due to the fact that these values, as stated previously, are strongly dependent upon conditions used for the measurement, (e.g., the frequency and other experimental parameters).\(^{25}\) For ZnO in particular this value appears to vary with morphology as well as with post-growth heat treatment.

In order to further confirm charge transfer between BiVO\(_4\) and ZnO in the heterojunction material, photoluminescence (PL) spectra were also recorded using a micro Raman laser (Figure 2b). The PL spectrum for bare BiVO\(_4\) displays an intense, broad peak at ca. 550 nm. The inset figure displays the PL spectrum of bare ZnO nanorods, with the broad peak centering at \(\approx 580\) nm corresponding to defect emissions or oxygen vacancies.\(^{33,34}\) It is obvious that the spectrum of 1D BiVO\(_4\)/ZnO heterojunction is broader, which can be fitted into two components. One is due to the luminescence of BiVO\(_4\) and the other related to ZnO. The PL peak centered at 560 nm exhibits a near 50% decrease in intensity with respect to pure BiVO\(_4\) film. The obvious quenching of luminescence of BiVO\(_4\) (approximately two times) is characteristic of charge transfer between the BiVO\(_4\) and ZnO, indicating that an efficient reduction in recombination of charge carriers in the 1D heterojunction material is taking place.

Following the indication by PL measurement and in order to observe the charge separation function of the single junction, the anodic current–voltage (\(I–V\)) performance was monitored for a 300 nm thick BiVO\(_4\)/900 nm ZnO heterojunction film in a 0.2 M Na\(_2\)SO\(_4\) solution (pH 6.5), under visible light (\(\lambda > 420\) nm) with AM 1.5G illumination. b) IPCE spectra for bare BiVO\(_4\) and single junction BiVO\(_4\)/ZnO measured at 1.2 V vs RHE.

![Figure 2](image1.png)

**Figure 2.** a) Mott-Schotky plots for BiVO\(_4\) nanoparticulates and ZnO nanorods measured in 0.2 M Na\(_2\)SO\(_4\) (pH 6.5) at 1 kHz. (b) PL spectrum of bare BiVO\(_4\) and 1D BiVO\(_4\)/ZnO heterojunction excited at a laser wavelength of 325 nm. The smooth red and green lines show the curve fitting for the individual component materials. The inset figure displays the PL spectrum of bare ZnO nanorods. Both indicate efficient charge rectifying effect by the ordered junction with the PL spectra decreased by nearly 50%.

![Figure 3](image2.png)

**Figure 3.** a) Current vs potential curve of a 300 nm BiVO\(_4\)/900 nm ZnO heterojunction film in a 0.2 M Na\(_2\)SO\(_4\) solution (pH 6.5), under visible light (\(\lambda > 420\) nm) with AM 1.5G illumination. b) IPCE spectra for bare BiVO\(_4\) and single junction BiVO\(_4\)/ZnO measured at 1.2 V vs RHE.
electrode for the first time under visible irradiation exhibits a steady photocurrent of $\approx 0.2$ mA cm$^{-2}$ at 1.2 V (vs RHE). It is nearly 8 times the photocurrent of the pure BiVO$_4$ film. The onset voltage also cathodically shifts from 0.6 V to approximately 0.2 V (vs RHE) compared to the pure BiVO$_4$. All these results promise a large pure energy output. The 8-fold increase in photocurrent compared to the sum of bare BiVO$_4$ and ZnO is only attributed to the enhanced visible absorption and charge separation by BiVO$_4$ and ZnO junction because there is no absorption by ZnO. Compared with the onset voltage of the similar metal oxide junction very recently reported, e.g., between BiVO$_4$ and WO$_3$ (0.1 V vs Ag/AgCl, pH 6.6)$^{[14]}$ which is similar to the pure BiVO$_4$ in the study, the onset voltage of the ordered BiVO$_4$/ZnO junction is 0.4 V smaller. A good performance in the low potential region is critical for widening the operating window and therefore achieving a high solar to fuel conversion efficiency. In order to assess the poor catalytic activity for water oxidation of BiVO$_4$ and confirm efficient charge transfer from BiVO$_4$ to ZnO, current–voltage curves for BiVO$_4$ and BiVO$_4$/ZnO were recorded in the presence of an efficient sacrificial electron donor in the form of sulphite ions (0.1 M Na$_2$SO$_3$) under visible light irradiation (Supporting Information Figure S3). Oxidation of sulphite is kinetically and thermodynamically more favourable than water oxidation$^{[19]}$ the photocurrent for BiVO$_4$ generated in the presence of sulphite ions increases dramatically to $\approx 1.25$ mA cm$^{-2}$ at 1 V vs RHE, nearly 5 times higher than that of BiVO$_4$ in the identical electrolyte. However the photocurrent of BiVO$_4$/ZnO junction increased only slightly (less than 10%) in the presence of sulphite at the same potential, which clearly indicates that the surface states in conjunction with recombination of charge carriers (due to low electron mobility)$^{[21]}$ are major limiting factors for photocurrent generation in BiVO$_4$ and the novel junction has a similar function to a hole scavenger, leading to efficient in situ electron-hole separation.

The photocurrent of the novel junction was also measured under full arc AM 1.5G illumination as a reference (Supporting Information Figure S4). Furthermore, under similar experimental conditions the value of 1.75 mA cm$^{-2}$ at 1 V (vs RHE) is much larger in comparison to the recently reported BiVO$_4$/WO$_3$ junction ($\approx 1$ mA cm$^{-2}$ at 1 V vs RHE)$^{[14]}$. The film thickness was optimized and the results for both bare BiVO$_4$ and heterojunction BiVO$_4$/ZnO electrodes with a 900 nm ZnO layer under full arc AM 1.5G illumination are summarized in Table S1, Supporting Information. It is noteworthy however, that upon increasing the thickness of the BiVO$_4$ layer the maximum measured photocurrent decreases, most probably due to comparatively longer charge carrier diffusion lengths in the thicker samples, which would increase the likelihood of recombination in the BiVO$_4$ layer. The stability of a photovoltaic junction BiVO$_4$/ZnO is shown in Figure 4. The light irradiation onto the photoelectrode was controlled using a mechanical chopper. Extremely good stability has been observed throughout the time frame with no apparent loss in current throughout the 180 min time period. BiVO$_4$ was less stable, with some gradual decrease over the time course, which resulted in 84% residual photocurrent even after 20 min measurement, in agreement with previous reports that bare BiVO$_4$ has limited stability.$^{[18,32]}$

No change in the BiVO$_4$/ZnO electrode was observed through SEM and XRD patterns recorded after the stability measurement (see Supporting Information Figure S5), inferring that the novel junction is stable under the present experimental condition. The reason for the relatively enhanced stability is very likely due to efficient charge separation and transport, which prevents the photocorrosion of the photoanode, similar to BiVO$_4$ coupled with FeOOH,$^{[38]}$ the detailed reason for which is currently being investigated.

Incident photon to current efficiency (IPCE) was measured in order to ascertain the light conversion efficiency of heterojunction BiVO$_4$/ZnO and compared to a bare BiVO$_4$ electrode and ZnO in Figure 3b. The IPCE of bare BiVO$_4$ is comparatively low at $\approx 4%$ at 410 nm, similar to other studies reporting films of similar thicknesses,$^{[35]}$ whereas heterojunction BiVO$_4$/ZnO is significantly higher at nearly 40% at 410 nm, nearly four times higher than the IPCE of bare BiVO$_4$. This again suggests that the rectifying electron transfer from BiVO$_4$ to ZnO likely inhibits fast recombination and increases the solar energy conversion efficiency of the junction. The IPCE is nearly zero at 550 nm, which is consistent with the sample’s optical absorption. Furthermore, a cobalt phosphate (Co-Pi) layer was introduced via photoassisted electrodeposition$^{[36]}$ onto the 300 nm BiVO$_4$/900 nm ZnO electrode to form a junction cascade. Its optical absorption is shown in Figure 1b, exhibiting a similar band-gap absorption to the BiVO$_4$/ZnO junction. Interestingly, a marked improvement in photocurrent has been observed, ($\approx 3$ mA cm$^{-2}$ at 1.2 V vs RHE, Figure 5a), compared with 1.8 mA cm$^{-2}$ (BiVO$_4$/ZnO) and 0.3 mA cm$^{-2}$ (BiVO$_4$) at 1.2 V vs RHE (Supporting Information Figure S4). It is also higher than the recorded photocurrent of modified BiVO$_4$ heterojunction electrodes recently reported (less than 2.5 mA cm$^{-2}$ at 1.2 V vs RHE)$^{[14,15]}$ and similar to that recorded for the benchmark Co-Pi/W:BiVO$_4$ junction recently reported ($\approx 3$ mA cm$^{-2}$ at 1.2 V vs RHE, TEC 15 substrate)$^{[38]}$. IPCE of the triple junction was also measured (Figure 5b), revealing an 18% increase in efficiency ($\approx 47%$ at 410 nm) compared to BiVO$_4$/ZnO described earlier.

Figure 4. Photocurrent stability measurement of a BiVO$_4$/ZnO bi-junction photoelectrode at an applied potential of 1 V (vs RHE).
enhancement by increasing the adhesion of Co-Pi on BiVO$_4$/ZnO. The photocurrent decreases a little after 3 hours. The stability was examined (Supporting Information Figure S6) and found that the Co-Pi/BiVO$_4$/ZnO film is stable under visible light irradiation ($\lambda > 420$ nm) for almost 12 times and 1.5 times the recorded photocurrent achieved by BiVO$_4$ single photoelectrode and BiVO$_4$/ZnO bi-junction, respectively. Moreover, the high conductivity and electron mobility in the ordered ZnO nanorods and the catalytic effect of Co-Pi play very important roles in increasing solar energy conversion efficiency apart from the in situ rectifying charge separation by the bi-junction structure. [40]

**3. Conclusions**

Overall, a novel material strategy has been proposed:- the highly ordered 1D Co-Pi/BiVO$_4$/ZnO triple junction for photoelectrochemical water splitting. Firstly, a high, steady photocurrent of £2 mA cm$^{-2}$ at 1.2 V (vs RHE) and a small onset potential of £0.2 V have been achieved for the 1D BiVO$_4$/ZnO junction photoelectrode under visible light irradiation ($\lambda > 420$ nm). An IPCE was measured that is almost eight times higher than that of the bare BiVO$_4$ at 410 nm. By the addition of Co-Pi on the BiVO$_4$/ZnO junction surface, an ordered triple junction has been achieved, leading to an extremely high photocurrent of £3 mA cm$^{-2}$ measured at 1.2 V vs RHE, which is nearly 12 times and 1.5 times the photocurrent achieved by BiVO$_4$ single photoelectrode and BiVO$_4$/ZnO bi-junction, respectively. Furthermore, it has been demonstrated for the first time, a high energy conversion efficiency of £0.88% for BiVO$_4$-based junction photoelectrode without the need of any scavengers. Photoluminescence spectra revealed emission quenching due to matching ZnO rods to BiVO$_4$ nanoparticles, together with flat-band measurements, indicative of efficient charge transfer and separation. This ordered Co-Pi/BiVO$_4$/ZnO junction cascade represents a simple but significant step in improving the solar energy conversion efficiency in BiVO$_4$ by effectively addressing the three limiting factors described in our introduction.
on the ZnO nanorods and furthermore, the selection of different low-cost co-catalysts which can speed up both water reduction and oxidation reactions. In addition, this material design strategy could also be used for other photocatalysts and solar cells where recombination and charge transport dominate energy conversion efficiency.

4. Experimental Section

**Film Growth:** Films of BiVO₄ were deposited onto FTO coated glass substrates (TEC 15, 35 Ω, Pilkington NSG) via a spray pyrolysis method. A 0.02 M solution of bismuth nitrate pentahydrate [Bi(NO₃)₃·5H₂O] (Sigma, 99.9%) and [VO(acac)₃] (Fisher, 99%) were dissolved in 2-methoxyethanol (Sigma, 99.9%) and sprayed directly onto the FTO glass at a temperature of 200 °C at a distance of 20 cm. The number of spray repetitions determined the overall film thickness; for a thickness of 300 nm approximately 220 spray repetitions were required using a 2 cm² spray nozzle. Films were subsequently annealed in air in a muffle furnace at 450 °C for 3 h. Prior to growth of ZnO nanorods, the FTO glass substrates were covered with three layers of ZnO seed crystals deposited via spray pyrolysis (same apparatus as above) from a 0.005 M zinc acetate-ethanol solution followed by heat treatment in air at 350 °C for 30 min. During spray treatment the substrate was kept at ambient temperature and the process carried out at least three times to obtain a conformal covering of ZnO seeds. 1D ZnO nanorod films were grown via an aqueous hydrolysis and condensation procedure(27) using 0.025 M aqueous solutions of zinc nitrate hexahydrate [Zn(NO₃)₂·6H₂O] and hexamethylenetetramine (HMT) onto the ZnO seed layer. ZnO nanorod films were grown using a water bath set at 90 °C for 4 h. Films were washed with cold deionized water, to remove excess HMT and unreacted or non-adherent particles. Heterojunction BiVO₄/ZnO electrodes were produced by spraying the bismuth-vanadium solution directly onto a ZnO nanorod film at 200 °C, followed by annealing in air at 450 °C for 3 h. Photoassisted electrodeposition of cobalt phosphate (Co-Pi) was carried out by the procedure previously reported using a three electrode cell (0.4 V vs Ag/AgCl, Pt counter electrode)(30) through immersion of the photoelectrodes in 0.3 mM cobalt nitrate in 0.1 M phosphate buffer at pH 7 under AM1.5 G illumination. The deposition time was 1500 s.

**Film Characterization:** The crystallographic phase(s) of these as-prepared products were determined by powder XRD in reflection geometry (Bruker D4, CuKα radiation source, λ = 1.5405 Å). The morphologies of the samples were observed by SEM (JSM-7401F, JEOL, 3 kV). The UV-vis absorption spectra were recorded using a UV-vis spectrophotometer equipped with an integrating sphere device (UV-2550, Shimadzu) at room temperature. Raman spectra were acquired using a Renishaw micro-Raman 1000 machine using either 325 nm (PL) or 442 nm (Raman) lasers at room temperature.

**Photoelectrochemical Measurements:** These were carried out using an Iviumstat potentiostat and associated Ivium software. A three electrode setup was utilized within a Pyrex glass cell sealed with a rubber stopper. A Pt wire mesh and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. An aqueous solution of 0.2 M Na₂SO₄ (with and without the addition of 0.1 M Na₂SO₃) was used as the electrolyte (pH 6.5) and was purged with argon gas for 15 min prior to use to remove any dissolved oxygen. The light source was a 150 W xenon lamp (Newport, USA) equipped with a standard AM 1.5G filter; the light intensity was measured using a silicon photodiode and a Newport handheld Optical Meter (Model 1918-R). Visible light experiments were conducted using a long-pass filter (λ > 420 nm, Newport). The scan rate was 10 mV s⁻¹ and the scanned range was −0.5 to +1.5 V (vs Ag/AgCl). The potential was converted to RHE (reference hydrogen electrode) potentials using E(RHE) = E(Ag/AgCl) + (0.059 × pH) + 0.197 V. Stability measurements (current-time) were conducted using an in-house built mechanical chopper. IPCE was measured with the aid of a monochromator, and calculated using the following equation:

\[ \text{IPCE}(\%) = \frac{\text{[1240 × photocurrent density]}}{\text{[wavelength × photon flux]}} \times 100\% \]

The solar energy conversion efficiency (η) was estimated using the following equation:(24)

\[ \eta(\%) = \frac{\text{[photocurrent density × (123 – E_{th})]}}{\text{[light intensity(AM1.5G)]}} \times 100\% \]

The semiconductor electrodes were irradiated through the FTO glass. Mott-Schottky (impedance) measurements were measured in 0.2 M Na₂SO₄ in the dark at a frequency of 960 Hz (1 KHz) and scan rate of 10 mV s⁻¹. The potential was measured against an Ag/AgCl reference electrode.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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