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Graphic abstract

Overall water splitting with STH efficiency exceeding 2.5% using an all-earth-abundant dual-photoelectrode device under parallel illumination without bias.
Solar-to-hydrogen Efficiency Exceeding 2.5% Achieved for Overall Water Splitting with All Earth-abundant Dual-photoelectrode

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The solar-to-hydrogen (STH) efficiency of a traditional mono-photoelectrode photoelectrochemical water splitting system has long been limited as large external bias is required. Herein, overall water splitting with STH efficiency exceeding 2.5% was achieved using a self-biased photoelectrochemical-photovoltaic coupled system consisting of all earth-abundant photoanode and Si-solar-cell-based photocathode connected in series under parallel illumination. We found that parallel irradiation mode shows higher efficiency than tandem illumination especially for photoanodes with wide light absorption range, probably as the driving force for water splitting reaction is larger and the photovoltage loss is smaller in the former. This work essentially takes advantage of tandem solar cell which can enhance the solar-to-electricity efficiency from another point of view.

Introduction

Photoelectrochemical (PEC) water splitting is one of the most promising strategies for solar fuel production.[1-5] Many materials with wide light absorption range such as BiVO$_4$,[6-11] Fe$_2$O$_3$,[12-14] Cu$_2$O,[15-16] Ta$_2$N$_5$,[17-21] LaTiO$_3$N,[22-23] and Si,[24-25] have been investigated as photoelectrodes in traditional mono-photoelectrode vs. Pt counter electrode systems. Despite of great efforts such as loading cocatalysts, doping with other elements, controlling morphologies, combining with other semiconductors and employing new fabrication methods to enhance the PEC performance of the photoelectrode, the solar-to-hydrogen (STH) efficiency for an individual photoelectrode is yet less than 1.8%, because large external bias is required for overall water splitting.[7-11, 14-21, 26-31] Therefore, it is highly desired to develop novel approaches for efficient PEC water splitting without external bias.

Construcitng dual-photoelectrode system to use the Fermi level difference ($\Delta E_F$) between them is a feasible solution. But it’s not easy to fabricate two photoelectrodes well-matched in the same electrolyte, and the STH efficiency reported so far is quite low (< 0.1%),[11, 32-35], because the photovoltage is usually too small to overcome the overpotential of the reaction at the electrode. Photovoltaic-electrolysis (PV-EL) technology is more efficient but usually requires complicated setups and solar cells with rather high open-circuit voltage ($V_{oc}$) of at least 2.0 V.[36-42] Moreover, the water splitting ability of the system is mainly determined by the $V_{oc}$ of the PV cell in a PV-EL system. However, if the PV cell is coupled with a semiconductor photoanode to construct a photovoltaic-PEC (PV-PEC) device, water oxidation reaction will take place on the photoanode surface, and thus the oxidant is the photogenerated hole whose energy can be very positive as it is determined by the valence band edge of the photoanode assisted by the PV cell. The most efficient PV-PEC system for water splitting reported so far consists of a p-GaInP$_2$ photocathode in contact with a GaAs solar cell connected with a Pt counter electrode.[43] While, these materials are high cost, toxic and unstable. In other reports, a solar cell was simply connected in the outer circuit of a PEC cell,[44-47], directly deposited with water splitting photocatalyst[48-50] or combined with photocatalysts in tandem[51, 52]. The efficiency of such a tandem or monolithic configuration is limited because it is difficult to optimize performances of solar cell and photocatalyst layers with complementary light absorption.[51-53] Although a high efficiency was achieved recently,[9] their device still has flaws: Firstly, the efficiency should be quiet low if other materials with a narrower band gap were used using their configuration; Secondly, the fabrication method of the semiconductor layer is limited as Si-cell cannot tolerate high temperature or any other harsh conditions; Lastly, the counter electrode they used is novel metal Pt which is unfavourable considering the cost.

Herein, we focus on the PV-PEC strategy which combines advantages of PEC and PV-EL systems. Overall water splitting with STH efficiency exceeding 2.5%, much higher than that of traditional mono-photoelectrode PEC and photocatalytic water splitting systems reported to date, was achieved with a self-biased dual-photoelectrode device. Coupling with semiconductor photoanode like BiVO$_4$, a Si solar cell (triple or double junction Si cell) was employed as photocathode. The decoupling of the PV cell and the PEC part in a PV-PEC system using a dual-photovoltaic configuration is convenient for the fabrication and optimization of them. And noble metal Pt electrode is avoided and all materials are earth-abundant and environmentally benign. Besides, illumination mode was found to be important for enhancing the efficiency of the system.
Results and discussion

Fig. 1 Schematic description of the dual-photoelectrode device photoanode vs. Si-solar-cell-based photocathode for direct PEC water splitting under parallel (Mode P) and tandem (Mode T) illumination.

Fig. 2 I-V curves of FeOOH/Mo:BiVO₄, Fe₂O₃ photoanodes vs. Ni/Si, in Modes P and T. Light source: AM 1.5G sunlight simulator (100 mW cm⁻²); Scanning rate: 10 mV s⁻¹; Electrolyte: 0.5 M sodium phosphate (pH 7); Electrode areas: FeOOH/Mo:BiVO₄ or Fe₂O₃ 1 cm² and Ni/Si 0.5 cm².

Fig. 1 schematically shows that a Si solar cell was applied as photocathode coupled with a photoanode in two illumination modes, one is parallel illumination (denoted as Mode P) with two beams of light and the other is tandem illumination (Mode T) with one beam of light incident from the photoanode side. Two Si solar cells (denoted as Siₐ and Siₐ, Fig. S1) with different Voc and comparable short-circuit currents Jsc were used for comparison, and Ni cocatalyst was deposited on the surface of the Si cell to protect it from corrosion in the electrolyte and reduce the proton reduction potential. Fig. 2 (a) shows that the Jsc are 2.69 mA and 0.63 mA, respectively, when coupling Siₐ with FeOOH/Mo:BiVO₄ photoanode in Modes P and T. The STH efficiency of Mode P calculated from Jsc is 2.21%, which is about 3 times of that of Mode T (0.77%). Similar results were obtained when changing the area of Siₐ (Fig. S2). The Voc of the coupled system in Mode P is 1.88 V which greater than that of Mode T, leading to the higher efficiency of Mode P. Fe₂O₃ photoanode was also coupled with Siₐ likewise in two modes. Fig. 2 (b) shows that the Jsc of the system in Modes P and T are 1.5 mA and 0.56 mA, respectively. The corresponding STH efficiency of Mode P is 1.8 times of that of Mode T. The Voc difference between Modes P and T is 0.5 V which brings about the big difference in STH efficiency. The comparison of the photocurrent under continuous irradiation between Modes P and T shows the same trend (Fig. S3).

Results in Fig. 3 can partly explain the efficiency difference between Modes P and T. As shown in Fig. 3 (a), the efficiency of Siₐ is dramatically reduced if the incident light is firstly absorbed by a photoanode. The Jsc of Siₐ drops from 9.4 mA to only 2.5 mA and 2.2 mA for FeOOH/Mo:BiVO₄ and Fe₂O₃, respectively. And the Voc is reduced by 0.14 V. The solid line is the average I-V curve of FeOOH/Mo:BiVO₄ (1 cm²) vs. Pt two-electrode system, and (b) UV-visible absorption spectra of Siₐ, Fe₂O₃, FeOOH/Mo:BiVO₄ photoanode. Electrolyte: 0.5 M sodium phosphate (pH 7); Light source: AM 1.5G sunlight simulator (100 mW cm²), Electrode area: Siₐ 1 cm².

Fig. 3 (a) I-V curves, Voc and Jsc of Siₐ under full spectrum illumination and illuminated behind FeOOH/Mo:BiVO₄, Fe₂O₃ electrodes, and the average I-V curve of FeOOH/Mo:BiVO₄ (1 cm²) vs. Pt two-electrode system, and (b) UV-visible absorption spectra of Siₐ, Fe₂O₃, FeOOH/Mo:BiVO₄ photoanode. Electrolyte: 0.5 M sodium phosphate (pH 7); Light source: AM 1.5G sunlight simulator (100 mW cm²), Electrode area: Siₐ 1 cm².

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540 nm and 620 nm, respectively, and SiA shows light absorption until 850 nm. Thus, after absorption and scattering by the photoanode, only a small portion of long wavelength photons are left for SiA, resulting in a great decrease of the efficiency of SiA. This suggests that the match of the light absorption of the photoanode and the solar cell is very important for achieving high efficiency of a PV-PEC device. In other words, illumination mode is important to optimize the efficiency. For photoanodes with wide light absorption range, dual-photoelectrode system under parallel illumination is demonstrated to be superior to those under tandem illumination and may be more efficient than the previous reported monolithic forms.\(^9\) Essentially, this is not contradictory to that tandem solar cell can enhance the solar-to-electricity efficiency but takes advantage of tandem solar cell technology from another point view.

**Table 1** Results of the analysis of the photovoltage loss of the coupled system SiA vs. FeOOH/Mo:BiVO\(_4\) and Fe\(_2\)O\(_3\) photoanodes in Modes P and T. V\(_{oc}\) is the open voltage of the coupled system, V\(_{oc-Si}\) is the open voltage of SiA itself, and V\(_{loss}\) is the photovoltage loss of the coupled system (V\(_{loss}\) = V\(_{oc-Si}\) - V\(_{oc}\)).

<table>
<thead>
<tr>
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<th>Mode P</th>
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<td>V(_{oc})/V</td>
<td>V(_{oc-Si})/V</td>
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<tr>
<td>SiA vs. FeOOH/Mo:BiVO(_4)</td>
<td>1.88</td>
<td>2.23</td>
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<td>SiA vs. Fe(_2)O(_3)</td>
<td>1.6</td>
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![Fig. 4](image-url) **Fig. 4** (a) short-circuit I-t curves of FeOOH/Mo:BiVO\(_4\) photoanode (1 cm\(^2\)) vs. Ni/SiA photocathode with different area(1, 1 cm\(^2\); 2, 0.45 cm\(^2\); 3, 0.2 cm\(^2\)) in Mode P, and (b) the I-V curve of the FeOOH/BiVO\(_4\)-porous photoanode (0.98 cm\(^2\)) vs. Ni/SiA (0.4 cm\(^2\)) in Mode P. Light source: AM 1.5G sunlight simulator (100 mW cm\(^{-2}\)); Scanning rate: 10 mV s\(^{-1}\); Electroyte: 0.5 M sodium phosphate (pH 7).

Table 1 shows the analysis of the photovoltage loss (V\(_{loss}\)) of SiA vs. FeOOH/Mo:BiVO\(_4\) and Fe\(_2\)O\(_3\) photoanodes in Modes P and T. For FeOOH/Mo:BiVO\(_4\), the measured V\(_{oc}\) of the device in Mode P (V\(_{oc-P}\)) is 1.88 V and the V\(_{oc}\) of SiA itself (V\(_{oc-Si}\)) is 2.23 V, thus the V\(_{loss}\) of the device in Mode P (V\(_{loss-P}\)) is 0.35 V. V\(_{loss}\) is composed of two parts: one is the bias required to overcome the overpotential and compensate for the energy efficiency of the photoanode for overall water splitting, the other is the voltage loss due to the resistances of the photoanode, the Si-cell, the electrolyte as well as photoelectrode-cocatalyst and electrode-electrolyte interfaces. We previously found that the minimum bias required for cocatalyst/BiVO\(_4\) photoanode to realize overall water splitting is about 0.3 V.\(^9\) Namely, the voltage loss due to the coupling between FeOOH/Mo:BiVO\(_4\) and SiA is negligible, only 0.05 V, indicating the successful coupling between the photoanode and SiA in Mode P. In contrast, the V\(_{loss}\) in Mode T (V\(_{loss-T}\) is 0.43 V, larger than V\(_{loss-P}\) by 80 mV. Similarly, V\(_{loss-T}\) is larger than V\(_{loss-P}\) by 360 mV in the case of Fe\(_2\)O\(_3\). And similar results were also obtained for WO\(_3\) photoanode (Table S1). Thus, it is inferred that more charge carriers are generated and survived after recombination in Mode P, which leads to a higher efficiency. This may be ascribed to the larger driving force V\(_{oc}\) and the better match of carrier flux between the photoanode and the photocathode in Mode P.

![Fig. 5](image-url) **Fig. 5** I-V curves of Ni/SiA or Ni/Sib vs. (a) FeOOH/Mo:BiVO\(_4\) (b) Fe\(_2\)O\(_3\), and (c) WO\(_3\) photoanodes in Mode P. Light source: AM 1.5G sunlight simulator (100 mW cm\(^{-2}\)); Scanning rate: 10 mV s\(^{-1}\); Electrolyte: 0.5 M sodium phosphate (pH 7); Electrode areas: FeOOH/Mo:BiVO\(_4\), Fe\(_2\)O\(_3\) and WO\(_3\) 1 cm\(^2\) and Ni/Si 0.5 cm\(^2\).

Fig. 3 also indicates that the photocurrent of SiA photocathode...
is much higher than that of the photoanode, which means the hole flux from Si is largely excessive to the electron flux from the photoanode. In order to optimize the efficiency of the system, the charge flux of two photoelectrodes should be matched via changing the ratio of electrode areas or thickness of the photoanode. Fig. 4 (a) shows that the STH efficiency (calculated from the average current in 2 h) increases from 1.27% to 1.51% when the area of Si is decreased from 1 cm² to 0.2 cm². On the premise of providing enough hole flux, smaller SiA means less light energy consumption and higher efficiency of the whole device. The efficiency of the system can also be improved if the photocurrent of the photoanode is increased. Fig. 4 (b) shows that the STH efficiency of the device FeOOH/BiVO₄-porous vs. Ni/SiA reaches 2.52% via using a more efficient FeOOH/BiVO₄-porous photoanode (Fig. S4) prepared as recently reported. Undoubtedly, the efficiency is expected to be higher if the PEC performance of the photoanode is further enhanced.

Since E_CB of BiVO₄ is only slightly lower than the proton reduction potential, another Si solar cell (SiB) with a smaller V_oc (1.22 V, Fig. S1) was coupled with FeOOH/Mo:BiVO₄ photoanode for comparison. Fig. 5 (a) that shows that the obtained photocurrent of the system with Ni/SiA is much lower than that with Ni/SiA, Fe₃O₄ and WO₃ photoanodes with more positive E_CB than BiVO₄ were also coupled with Ni/SiA and Ni/SiB respectively. As shown in Fig. 5 (b, c), the J_sc of Fe₃O₄ vs. Ni/SiA is nearly 9 times of that of using Ni/SiB. That is because Fe₃O₄ has a large overpotential for water oxidation and a large external bias is required. Fig. 5 (c) shows that WO₃, the J_sc of the system with Ni/SiA is also higher than that of using Ni/SiB. In brief, efficient overall water splitting can also be achieved using a Si cell with V_oc below 1.23 V, which is impossible in PV-EL system. While SiB with smaller V_oc will result a low efficiency if the E_CB of the photoanode is too positive or the water oxidation overpotential is too large. In this case, loading efficient cocatalysts on the photoelectrode will be necessary to enhance the photocurrent and reduce the overpotential for higher efficiency.

Gas evolutions from the FeOOH/Mo:BiVO₄ vs. Ni/Si-cell system were determined. Fig. 6 (a, b) shows that H₂ and O₂ can be produced efficiently from the system in stoichiometric ratio without external bias. To evaluate the contribution of the photoanode in the PV-PEC system, we replaced it with a CoPi electrode which has been developed as one of the most efficient water oxidation electrocatalysts in neutral phosphate electrolyte. Fig. 6 (c, d) shows that the activity of the resulting PV-EL system CoPi vs. Si-cell is much lower than that of FeOOH/Mo:BiVO₄ vs. Ni/Si-cell. The STH efficiency of FeOOH/Mo:BiVO₄ vs. Ni/Si-cell photoanode is about 3 (for Ni/SiA) and 8 (for Ni/SiB) times of that of using CoPi, indicating the potential advantage of PV-PEC systems over PV-EL systems.

To reveal the role of the Si-cell in the coupled system, we replaced the Si-cell with a Pt modified p-Si photocathode (Pt/p-Si NW) fabricated from a Si single crystal wafer as schematically shown in Fig. 7 (a). The V_oc of the dual-photoelectrode system is 0.31 V and the J_sc is 20 μA (Fig. 7(b)), indicating that photoelectrons can transfer from the photoanode to the photocathode without external bias but the STH efficiency is only about 0.01%, much lower than that of using Si-cell photocathode. Fig. 7 (c, d) shows that O₂ and H₂ can be produced from the FeOOH/Mo:BiVO₄ vs. Pt/p-Si NW system under a bias of 0 V or 0.2 V, but the activities are quite low. And the H₂O₂ ratio deviates from stoichiometric value due to the corrosion of p-Si and the H₂ evolution even exceeds the amount of e/2 probably because of the reaction of Si with H₂O and reverse reactions. When using the Pt/TiO₂/Ti/p-Si electrode which is more active and corrosion resistant, the activity is still low despite a slight increase (Fig. S5). The reason may be that the driving force ΔE between two photoelectrodes is too small and limits the efficiency of the whole system. In contrast, in the PV-PEC system, the photovoltage generated from the PEC and PV systems can easily meet the requirement for overall water splitting reaction.
phosphate (pH 7); Electrode areas: FeOOH/Mo:BiVO₄ 1 cm² and Pt/p-Si photocathode 1 cm². Scanning rate: 10 mV s⁻¹.

Conclusions

A self-biased dual-illumination PEC device consisting of a semiconductor photoanode and a Si-solar-cell based photocathode connected in series was constructed for overall water splitting. The STH efficiency of the FeOOH/BiVO₄ vs. Si-cell system can exceed 2.5%, much higher than that of traditional mono-photoelectrode PEC and photocatalytic water splitting systems to date. In this configuration, noble metal electrode is avoided and all materials are earth-abundant and environmentally benign. And the decoupling of the PV cell and the PEC part using a dual-photoelectrode configuration is convenient for the fabrication and optimization of them. It is found that parallel illumination mode shows higher efficiency than tandem irradiation for photoanodes with wide light absorption range, probably as the driving force for water splitting reaction is larger and the photovoltage loss is smaller in the former. This indicates that a dual-photoelectrode PV-PEC device under parallel illumination is superior to those in tandem or monolithic forms.

From another point of view, this work essentially takes advantage of tandem solar cell technology which can enhance the solar-to-electricity efficiency. Besides, the efficiency is obviously decreased when the photoanode is replaced by a CoPi electrode or when Si-cell is substituted by a p-Si photocathode. This clarifies roles of the photoanode and the solar cell in the coupled system and demonstrates the potential advantage of PV-PEC systems over PV-EL systems.

Experimental Section

All chemicals were analytical grade and were used as purchased without further purification. Solutions were prepared using high purity water (resistivity > 18 MΩ cm). The FTO (fluorine-doped tin oxide, < 14 Ω/square) conductive glass was purchased from Nippon Sheet Glass Company (Japan) and was ultrasonically cleaned with acetone, isopropanol, ethanol and deionized water for 20 min each prior to use.

Fabrication of Ni/Si-cell, FeOOH/Mo:BiVO₄, Fe₂O₃, WO₃, CoPi, and Pt/p-Si electrodes: Si solar cells used for photocathode fabrication are commercial Si solar cells (Hanergy Manufactory, Company). Two types of Si-cell with different V₆₃ and J₆₃ (Fig. S1): one is triple-junction Si₆₃ composed of one layer of amorphous Si and two layers of nanocrystal Si and the other is double-junction Si₆₃, were used. The anode side of the Si-cell was connected with the photoanode using Cu wire and Ag conductive adhesive. The cathode side is deposited with Ni cocatalyst (about 100 nm in thickness) by d.c. reactive magnetron sputtering. The Si-cell was illuminated from FTO side. Mo:BiVO₄ electrodes were prepared by a modified electrodeposition method.[10, 54] To stabilize and enhance the PEC performance, FeOOH cocatalyst was deposited on the surface of Mo:BiVO₄ photocathode via PEC oxidation of FeCl₂·xH₂O (99%, Alfa Aesar)[10] (Fig. S4, Electronic Supplementary Information). The FeOOH/BiVO₄-porous electrode was prepared as recently reported.[10] Fe₂O₃ electrodes were prepared by chemical bath deposition and annealing method, WO₃ electrodes were fabricated by d.c. reactive magnetron sputtering system, and CoPi electrodes were prepared by electrodeposition (Electronic Supplementary Information). Pt/p-Si NW and Pt/TiO₂/Ti/p-Si photocathodes were prepared from p-Si (100) wafers as reported[57–58], and both of them show high cathodic photocurrent (Fig. S5, S6).

PEC characterizations and measurements of gas evolutions: Photocurrent measurements were performed in a two-electrode cell with Pt (2 cm × 3 cm) or a three-electrode setup with SCE reference electrode (0.242 V vs. NHE). The electrolyte was purged with Ar for 30 min before PEC measurements and bubbled with Ar during the tests. The light source was an AM 1.5G sunlight simulator (100 mW cm⁻²) unless otherwise stated. Measurements of gas evolutions were carried out in a two-electrode cell as reported before.[54] STH efficiencies were calculated according to equation (1) supposing the Faradic efficiency (ηₚ) is 100%:

$$S T H = \frac{\eta_p \times J_{sc} (mA) \times 1.23 V}{100 \, mW \cdot cm^{-2} \times (Area_{sc} (cm^2) + Area_{an} (cm^2))} \times 100\%$$

(1)

Acknowledgements

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Notes and references


[14] Scott C. Warren; Kizion Volotov; Ben Donot; Celine M. Leroy; Maurin Cornuz; Francoico Stellacci; Cecile Hebert; Avner Rothschild; Michael Gratzel. Identifying champion nanostructures for solar-water-splitting, Nature Materials, 2013, 12, 842-849.


