Efficient solar-driven water splitting by nanocone BiVO₄-perovskite tandem cells

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Bismuth vanadate (BiVO₄) has been widely regarded as a promising photoanode material for photoelectrochemical (PEC) water splitting because of its low cost, its high stability against photocorrosion, and its relatively narrow band gap of 2.4 eV. However, the achieved performance of the BiVO₄ photoanode remains unsatisfactory to date because its short carrier diffusion length restricts the total thickness of the BiVO₄ film required for sufficient light absorption. We addressed the issue by deposition of nanoporous Mo-doped BiVO₄ (Mo:BiVO₄) on an engineered cone-shaped nanostructure, in which the Mo:BiVO₄ layer with a larger effective thickness maintains highly efficient charge separation and high light absorption capability, which can be further enhanced by multiple light scattering in the nanocone structure. As a result, the nanocone/Mo:BiVO₄/Fe(Ni)OOH photoanode exhibits a high water-splitting photocurrent of 5.82 ± 0.36 mA cm⁻² at 1.23 V versus the reversible hydrogen electrode under 1-sun illumination. We also demonstrate that the PEC cell in tandem with a single perovskite solar cell exhibits unassisted water splitting with a solar-to-hydrogen conversion efficiency of up to 6.2%.

INTRODUCTION

Hydrogen (H₂) is a clean and renewable fuel that could be produced by a photoelectrochemical (PEC) water-splitting cell in which semiconductors convert water directly to hydrogen from sunlight (1–4). Over the past few decades, extensive efforts have been invested to explore oxide-based photoanodes for use in PEC cells because of their relatively good stability in resisting oxidative photocorrosion and their low-cost fabrication (5–12). Bismuth vanadate (BiVO₄) is one of the most important photoanode materials because of its relatively narrow band gap of 2.4 eV and its adequate conduction band edge position relative to the H₂O/H₂ evolution level (13–16). However, the demonstrated solar-to-hydrogen (STH) conversion efficiency of the material to date is low (<2%), which is largely hindered by its short carrier diffusion length. Generally, the effective thickness of a photoelectrode film is determined by the carrier transport lifetime. To compensate for the short carrier diffusion length reduces the total thickness of the BiVO₄ film required for sufficient light absorption. To compensate for the short carrier transport lifetime. To compensate for the short carrier diffusion length. The strategy of maintaining efficient charge separation and provide a large contact surface area at the electrode/electrolyte interface to promote the surface water oxidation process. We report here a facile strategy for the deposition of an approximately 700-nm-thick nanoporous Mo-doped BiVO₄ (Mo:BiVO₄) layer on an engineered cone-shaped nanostructure and demonstrate that the unique photoanode achieves a remarkable water-splitting photocurrent at low applied voltage with the best-reported STH conversion efficiency to date. Our study presents the first successful case for realizing a thick nanoporous photoabsorption layer with highly efficient charge separation through the engineered cone-shaped nanostructure and solves the urgent issue concerning the incompatibility of light absorption capability with carrier transport length. The strategy of depositing photoactive materials on the engineered light-trapping architectures offers a new photoelectrode architecture for high-performance PEC water-splitting cells.

RESULTS

The thickness of the BiVO₄ photoelectrode film for water splitting is generally limited by the hole diffusion length of around 100 nm and the film’s poor electron transport properties (23). The thick photoelectrode film results in insufficient light absorption. Our strategy for depositing a nanoporous BiVO₄ on a conductive nanocone substrate is an effective approach to increasing the thickness of the BiVO₄ electrode film. The light absorption capability in this unique structure is significantly enhanced not only by the relatively thick nanoporous BiVO₄ film but also by the multiple light scattering in the nanocone structure. In addition, the conductive nanocone substrate can achieve efficient charge collection for the relatively thick film (Fig. 1).

The fabrication of the nanoporous Mo:BiVO₄ on top of light-trapping nanocone architectures for PEC water-splitting cells is a two-step process. Figure 2A shows the fabrication process of the conductive nanocone architecture (see Materials and Methods) (24). The first step is the fabrication of the conductive nanocone substrate.
The BiVO₄ film can be increased by introducing the nanocone arrays as photoelectrode film before reaching the electrode. However, the ties. A large proportion of photoexcited electrons recombine in the flat substrate and the conductive nanocone substrate. Some exposed nanocones were also marked via Cl₂-based RIE of the Si substrate. The subsequent third process is to prepare conductive nanocone substrates by coating one layer of Pt and another functional layer of SnO₂. The final step is to deposit the nanoporous BiVO₄ photoactive layer through a sol-gel process. (Fig. 2C) The ultraviolet-visible (UV-VIS) absorption spectra (Fig. 3A) show that the light absorption on the nanocone substrate is much stronger than that on the FTO-coated glass, indicating strong light trapping in the nanocone substrate. The band gap of the nanoporous Mo:BiVO₄ is approximately 2.4 eV (fig. S8), which is similar to previous reports (15, 25, 26). The experimental results are in agreement with those obtained from finite-difference time-domain simulations (Fig. 3B).

To further shed light on how light is coupled into the nanocone structure, we plotted the cross-sectional electric field intensity (|E|) distribution of the electromagnetic (EM) wave at 500 nm (Fig. 3B). Because the distance between neighboring nanocone arrays is close to the incident light wavelength, the incident light becomes diffracted and the EM wave redistributes in the nanocone area, resulting in a significant enhancement of EM field around the nanocone structure. The yellow and red hot area in the porous Mo:BiVO₄ representing strong light absorption on the nanocone substrate is much greater than that on the FTO-coated glass, denoted by the darker color above the nanocone. The approximately 1000-nm-thick amorphous Si was deposited on quartz- or F-doped SnO₂ (FTO)-coated glass substrates using the AJA sputtering system. Then, SiO₂ nanoparticles with a diameter of 500 nm were assembled to form a close-packed monolayer on top of the glass/Si thin film using the Langmuir-Blodgett (LB) method. The diameter and spacing of the SiO₂ nanoparticles can be adjusted to form a mask for the Cl₂-based reactive ion etching (RIE) process. Si nanocone arrays were formed after the RIE process (fig. S1). The SEM images show that each nanocone has a height of ~600 nm. The base and tip diameters of these nanocones are approximately 300 and 50 nm, respectively. Magnetron sputtering of Pt, followed by the coating of thin SnO₂ using the ultrasonic spray pyrolysis (USP) method, was used to create conductive nanocone arrays on the glass substrate (Fig. 2B and fig. S2). The thin SnO₂ layer plays an important role in forming a staggered band gap alignment feature with Mo:BiVO₄ (fig. S3). In general, the band alignment feature in semiconductors facilitates efficient electron-hole separation for light harvesting.

For comparison, the Mo:BiVO₄ on conductive flat substrates with the same thickness was also prepared (fig. S4).

To confirm the light trapping of the nanocone structures, we first investigated their optical properties after nanoporous Mo:BiVO₄ deposition. The ultraviolet-visible (UV-VIS) absorption spectra (Fig. 3A) show that the light absorption on the nanocone substrate is much stronger than that on the FTO-coated glass, indicating strong light trapping in the nanocone substrate. The band gap of the nanoporous Mo:BiVO₄ is approximately 2.4 eV (fig. S8), which is similar to previous reports (15, 25, 26). The experimental results are in agreement with those obtained from finite-difference time-domain simulations (Fig. 3B).

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light source above $Z = 1.3 \ \mu m$, indicating that more light has been trapped in the nanocone structure. The EM field around the Mo:BiVO$_4$ has been significantly enhanced, leading to more efficient absorption by the photocative material.

The excellent light absorption capability of the nanocone structures is essential for high-performance PEC water-splitting cells. Figure 4A shows the typical photocurrent-potential ($J$-$V$) curves [V is with respect to the reversible hydrogen electrode (RHE); $E$(RHE) = $E$(Ag/AgCl) + 0.1976 V + 0.059 pH] of Mo:BiVO$_4$ films on the nanocone substrate and the FTO-coated glass substrate. Upon sweeping the potential from 0.2 to 1.5 V versus RHE under 1-sun illumination (100 mW cm$^{-2}$), it can be clearly seen that the Mo:BiVO$_4$ deposited on the nanocone substrate showed a photocurrent density of 4.18 ± 0.25 mA cm$^{-2}$ at 1.23 V versus RHE, which is almost two times higher than that on the flat one (2.10 ± 0.14 mA cm$^{-2}$). The photocurrent is among the highest achieved with BiVO$_4$ without using a hole scavenger and an oxygen evolution reaction (OER) catalyst (26–29). The highest applied bias photon-to-current efficiency (ABPE) of ~0.74% was reached at a high voltage of 0.87 V versus RHE (fig. S9). The high voltage is a sign of low fill factor and high photocurrent onset potential due to the intrinsic poor catalytic activity of BiVO$_4$ for water oxidation. The issue can be addressed by incorporating an OER catalyst into BiVO$_4$.

Before the deposition of the catalyst, the optimized nanocone/Mo:BiVO$_4$ photoanode was first investigated in the same phosphate buffer solution containing 0.5 M sodium sulfite (Na$_2$SO$_3$) as the hole scavenger. Figure 4B shows its $J$-$V$ curve for sulfite oxidation. The oxidation of sulfite is thermodynamically and kinetically more favorable than water oxidation (30). The photocurrent for sulfite oxidation is independent from that for PEC water splitting as a result of the poor water oxidation kinetics of BiVO$_4$. The results show that a photocurrent density of 3.45 ± 0.30 mA cm$^{-2}$ was achieved at a potential of as low as 0.54 V versus RHE, and 6.05 ± 0.30 mA cm$^{-2}$ (80.7% of the theoretical value of BiVO$_4$ with a 2.4-eV band gap) was achieved at a potential of 1.23 V versus RHE.

As reported previously, the photocurrent onset potential of BiVO$_4$ for oxygen evolution can be cathodically shifted by 0.1 to 0.3 V with an OER catalyst (for example, FeOOH, FeOOH/NiOOH, and Co-Pi) (14, 27, 29). Meanwhile, the OER catalysts play an important role in the rapid increase in photocurrent at relatively low potential, which represents an improved fill factor. They have also been proven to effectively suppress photocorrosion under illumination, resulting in an improved stability of photanodes. Therefore, an active OER catalyst of Fe(Ni)OOH was prepared on a nanoporous Mo:BiVO$_4$-absorbed layer using a facile two-step electrochemical deposition technique (see Materials and Methods). The transmission electron microscope (TEM) image in fig. S10 clearly shows that the Fe(Ni)OOH layer was homogeneously deposited on the surface of Mo:BiVO$_4$ particles. Energy-dispersive x-ray (EDX) spectrum further confirms the successul coating of the Fe(Ni)OOH layer on Mo:BiVO$_4$ particles (fig. S10).

Figure 4B shows a significant photocurrent improvement for water oxidation achieved with the coating of the Fe(Ni)OOH layer. The optimized nanocone/Mo:BiVO$_4$/Fe(Ni)OOH photoanode reached a photocurrent density of 5.82 ± 0.36 mA cm$^{-2}$ at 1.23 V versus RHE, which approaches ~77.8% of the theoretical value. A cathodic shift of the photocurrent onset potential by ~0.10 V and a rapid photocurrent increase from 0.3 to 0.6 V versus RHE resulted in the highest ABPE of ~2.05% at 0.62 V versus RHE (fig. S8). The performance is slightly lower than expected from sulfite oxidation (Fig. 4, B and C) but is almost the best reported for BiVO$_4$-based PEC cells to date (14, 29). The result is further demonstrated using incident photon-to-electron conversion efficiency (IPCE) measurements (Fig. 4C).

The nanocone/Mo:BiVO$_4$/Fe(Ni)OOH photoanode for water oxidation shows that the IPCE value is more than 75% below 460 nm, which is slightly lower than the value of the nanocone/Mo:BiVO$_4$ photoanode for sulfite oxidation (>82% below 460 nm), in accordance with the $J$-$V$ measurements. In addition, the optimized nanocone/Mo:BiVO$_4$/Fe(Ni)OOH photoanode is stable under water oxidation conditions, which is demonstrated through a 5-hour stability test (fig. S11).

To further understand the charge transport effect of the nanocone structure on PEC performance enhancement, measurements of Mo:BiVO$_4$ on the conductive flat substrate and on the nanocone substrate with the same film thickness of ~700 nm (see Fig. 2 and fig. S4) were performed in a 0.5 M phosphate (pH 7) buffer solution containing 0.5 M Na$_2$SO$_4$. The thick Mo:BiVO$_4$ on the flat substrate only delivered a photocurrent density of 2.93 ± 0.12 mA cm$^{-2}$ at 1.23 V versus RHE, which is much smaller than that on the nanocone substrat (6.05 ± 0.30 mA cm$^{-2}$) (fig. S12), suggesting that a large proportion of photogenerated carriers recombine in the flat photoelectrode film before reaching the electrode. In other words, charge transport in the nanocone structure remains efficient despite the thick Mo:BiVO$_4$ layer as a result of the shortened carrier diffusion length induced by the conductive nanocone arrays (Fig. 1).

The remarkable angular-independent light-scattering capability is another important feature for the nanocone structure. Nanocone structures have shown a promising light-trapping capability over a
A broad range of wavelengths and incident angles (19, 20, 31–33). Figure 4D shows the achieved photocurrent at 1.23 V versus RHE as a function of incident light. Compared to the 29.4% loss for Mo:BiVO₄ on the flat substrate, the photocurrent density for the nanocone substrate only dropped by 8.1% with the largest irradiation angle (60°). The results demonstrate that the nanocone structure has an omnidirectional light-harvesting capability, which is highly favorable for practical applications.

The ABPE of the nanocone/Mo:BiVO₄ photoanode was calculated using a chopped J-V curve obtained in a two-electrode configuration (fig. S13). The maximum ABPE of ~1.92% was achieved with a water-splitting photocurrent of ~3.21 mA cm⁻² at a low applied voltage of 0.63 V, which is close to that obtained in a three-electrode configuration (~2.05%). We also evaluated reproducibility by testing batches of the photoanodes, and their ABPE distribution is shown in fig. S14. The ABPE ranges between 1.75 and 1.92%, indicating the reproducibility of our designed photoanodes. The photoanode with high efficiency at low applied voltage is certainly highly preferable for achieving self-biased operation in tandem with other photovoltaics.

A perovskite solar cell (PSC) is a promising candidate for tandem devices because of its high potential and high efficiency. The PSC was prepared following our previous work (34). The PSC could deliver a stable power conversion efficiency of ~15.5% under 1-sun irradiation (fig. S15). To construct a PSC-PEC tandem device, we used a beam splitter to separate a standard solar cell (1 sun) into two light beams (see Materials and Methods and Fig. 5A). Figure 5B shows separately measured J-V curves of the PSC and the PEC cells with intersection.
points at 5.01 mA. The photocurrent corresponds to the theoretical STH efficiency of 6.2%. A similar tandem design based on a PEC cell made of Fe₂O₃ and a PSC has been reported with an efficiency of only 2.4% (35). The performance of our device is more than two times higher because a more efficient PEC cell based on Mo-doped BiVO₄ nanocones was used. Although some studies have reported using solar cells to split water with more than 10% efficiency (36–38), such devices are based on solar cells connecting with nonphotoactive catalytic electrodes. In principle, they are single-junction devices. According to the well-known Shockley-Queisser limitation, their theoretical maximum solar conversion efficiency is ~34%. In contrast, our design is a double-junction device that is made up of a combination of a photoactive PEC cell and a PSC. Double-junctions device have a higher theoretical maximum efficiency of more than 45%. Although the efficiency we have demonstrated in this work is only 6.2%, our device has much room for further improvement in the future.

A stability test of the tandem device was performed over 10 hours (Fig. 5C). It showed only 5.8% decay, indicating decent stability for water oxidation of our PEC-PSC tandem cell. The stability also further demonstrates the stable PSC with inorganic charge extraction layers (34). After 10 hours of PEC test, the morphology of the Mo:BiVO₄/Fe(Ni)OOH does not change significantly (fig. S16), which is ascribed to the protection of the Fe(Ni)OOH layer against the photocorrosion of Mo:BiVO₄ (23). H₂ and O₂ production was detected with gas chromatography (GC) (fig. S17). The molar ratio of the produced H₂/O₂ was close to 2:1. The amount of generated H₂ is ~85.5 μmol cm⁻² hour⁻¹, corresponding to a photocurrent-to-H₂ Coulombic efficiency of ~92% for the tandem device. The slight deviation is likely due to our imperfect manual sampling method of H₂ for GC analysis.

**DISCUSSION**

In summary, we have reported a facile approach for the deposition of a nanoporous Mo:BiVO₄ layer on an engineered cone-shaped nanophotonic structure. After deposition of Fe(Ni)OOH, the photoanode can...
deliver a remarkable photocurrent density of 5.82 ± 0.36 mA cm⁻² at 1.23 V versus RHE. The photoanode in tandem with a single PSC produced a photocurrent of 5.01 mA cm⁻², corresponding to the theoretical STH efficiency of 6.2%. Our study presents the first successful case for realizing a nanoporous photoabsorption layer with highly efficient charge transport through depositing the material on the engineered cone-shaped nanostructure. The significant advance demonstrated here indicates that the deposition of photoactive materials on an engineered light-trapping architecture offers a new avenue for efficient PEC water splitting as well as for high-efficiency photovoltaic cells.

**MATERIALS AND METHODS**

**Preparation of the conductive nanocone substrate**

Si nanocone arrays on quartz- or FTO-coated glass substrates were first fabricated on the basis of our previous report (24, 31). A 1-μm-thick amorphous Si film was grown using the Aja spattering system on quartz- or FTO-coated glass substrates. SiO₂ nanoparticles with a diameter of 500 nm were then assembled using the LB method, giving rise to one close-packed monolayer on top of the Si thin film. Monodisperse SiO₂ nanoparticles with a diameter of 500 nm were produced by a modified Stober synthesis (31). Before the LB deposition of the monolayer, these nanoparticles were modified with aminopropyl methyldiethoxysilane so that they could be terminated with positively charged amine groups to prevent aggregation. The diameter and spacing of the nanospheres were tuned by selective and isotropic RIE on the basis of fluorine chemistry using CHF₃. These shrunk silica nanoparticles were then used as an etch mask during a Cl₂-based RIE process to fabricate nanocones in one step. The formed Si nanocone arrays were oxidized at 650°C for 10 hours to generate SiO₂ nanocone arrays. An 80-nm-thick Pt layer and an approximately 50-nm-thick SnO₂ layer were subsequently coated on SiO₂ nanocone arrays, respectively, through magnetron spattering and the USP method. More details can be found in our previous work (20, 21).

**Preparation of nanoporous Mo-doped BiVO₄ on the conductive nanocone substrate**

A precursor solution for the preparation of BiVO₄ photoelectrodes contains 0.5 M bismuth nitrate and 0.6 M vanadyl isopropoxide in acetylacetonate and ethanol [50:50 (v/v)]. The precursor solution was deposited on the nanocone substrates or the FTO-coated glass substrates using a controllable spin-coating technique. BiVO₄ photoelectrodes were obtained by annealing the samples at 300°C for 1 hour and at 450°C for 2 hours with a ramping rate of 2°C/min. Excess V₂O₅ was removed in 1 M NaOH solution at 50°C for 15 min with gentle stirring. The resulting BiVO₄ photoelectrodes were rinsed with water for several times to remove the residue solution and then air-dried at room temperature. A certain amount of (NH₄)₂MoO₄ dissolved in acetylacetonate and acetic acid, which served as doping sources, was added in the above precursor solution. The highest photocurrent of Mo:BiVO₄ photoelectrodes was obtained with a Mo-doping concentration of ~3%.

**Electrodeposition of Fe(OH)₂/Ni(OH)₂.** The Fe(OH)₂/Ni(OH)₂ nanoparticles were prepared by a facile two-step electrochemical deposition technique. The deposition was conducted in a three-electrode setup, with nanoporous Mo:BiVO₄ as the working electrode, saturated calomel electrode (Accumet, Fisher Scientific) as the reference electrode, and platinum wire as the counter electrode in a freshly prepared solution of 50 mM (NH₄)₂Fe(SO₄)₂ and 50 mM Ni(NO₃)₂. The electrodeposition of Fe(OH)₂/Ni(OH)₂ was first applied at −0.5 V in a 50 mM (NH₄)₂Fe(SO₄)₂ aqueous solution for 2 min and was then applied at −0.45 V in a 50 mM Ni(NO₃)₂ aqueous solution for another 2 min. After electrodeposition, the electrode was rinsed with water several times to remove the residue solution and then air-dried at room temperature. When irradiated by sunlight, the photogenerated holes from Mo:BiVO₄ convert Fe(OH)₂/Ni(OH)₂ into FeOOH/NiOOH [Fe(Ni)OOH], which will promote the OER.

**Optical measurements**

Standard hemispherical measurements were carried out with an integrating sphere (Newport). More details can be found in our previous paper (31). FTO glass was used as the reference for these absorption measurements. To construct a PEC-PSC tandem, a standard solar light (1 sun) was separated into two beams by a beam splitter (515 nm). The light beam (<515 nm) was used for testing the performance of PEC cells, and the other light beam was used for measuring the performance of PSCs.

**PEC measurements.** Mo:BiVO₄ photoelectrodes were used as the working electrode, a Pt net served as the counter electrode, and an Ag/AgCl was used as the reference electrode. All electrodes were immersed in a quartz electrolytic cell; the photoelectrode was covered by ethylene oxide except for a window for light illumination. All illuminated areas were 0.25 cm². The simulated solar illumination was obtained by passing light from a 300-W Xe arc lamp through a water filter (infrared filter), neutral density filters, or an AM 1.5-G filter. The power density of the incident light was calibrated to 100 mW/cm² by using a thermopile detector and a National Renewable Energy Laboratory–certified reference cell. Photocurrent measurements were performed in a 0.5 M potassium phosphate (KH₂PO₄) buffer solution (pH 7) with or without 0.5 M Na₂SO₃ as a hole scavenger [reported with respect to the RHE; E(RHE) = E(Ag/AgCl) + 0.1976 V + 0.059 pH]. Ar gas was purged through the cell during the measurement to instantaneously flush away O₂ from the working electrode. J-V curves were measured by sweeping the potential to the positive direction with a scan rate of 20 mV s⁻¹. J-V curves were also obtained with chopped illumination to examine transient photocurrents. IPCE spectra were measured using the Zahner ZENNIUM CIMPS system. IPCE was measured at the reversible water oxidation potential of 1.23 V versus RHE in 0.5 M phosphate buffer (pH 7) using the same three-electrode setup described above for photocurrent measurements.

The efficiency (η) for a water-splitting photoelectrode that requires an applied bias can be evaluated using the equation

\[ \eta = \frac{I(1.23 - V_{app})}{P_{light}} \]

where \( V_{app} \) is the applied voltage versus RHE, \( I \) is the externally measured current density, and \( P_{light} \) is the power density of the illumination.

The overall water-splitting efficiency (\( \eta \text{STH} \)) of the photoelectrolysis system is estimated by overlapping the individual J-V curve obtained for a PSC and a photoanode and can be calculated using

\[ \eta \text{STH} = 1.23 \cdot \frac{J_{OP}}{P_{light}} \]

where \( J_{OP} \) is the maximum operating current density for the integrated PEC system, which is the current density at the intersection of the two J-V curves.
H₂ and O₂ measurements were carried out in the airtight cell using GC to analyze the headspace. The amounts of H₂ and O₂ gas evolved were determined by taking 1 ml of gas from the headspace of the cell using a syringe and injecting it into the gas-sampling loop of the GC every hour.

**SUPPLEMENTARY MATERIALS**

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**REFERENCES AND NOTES**


Acknowledgments

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