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Broader context statement

High-efficiency unbiased water splitting with photoanodes harnessing polycarbazole hole transport layers

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Photoelectrochemical (PEC) water splitting is a promising technology to produce green hydrogen without a carbon footprint. High solar-to-hydrogen (STH) conversion efficiency and long-term stability of tandem devices must be secured for the commercialization of the PEC approach. Bismuth vanadate (BiVO₄), providing a large photovoltage, has been considered an excellent photoanode material for tandem devices, but the nanostructuring and hole transport layers (HTL) are inevitable to overcome its charge recombination issue. However, it is very challenging not only to explore the HTL material with suitable band structures for BiVO₄, but also to uniformly coat it on the nanostructure. Here, we demonstrate a conjugated polycarbazole framework (CPF-TCB) as a new hole extraction layer for the nanoporous molybdenum-doped BiVO₄ photoanode for unassisted solar hydrogen production. Intimately contacted CPF-TCB/Mo:BiVO₄ heterostructure forms type II band alignment reinforcing charge separation. After loading a cocatalyst, the NiFeCoOₓ/CPF-TCB/Mo:BiVO₄ photoanode combined with a perovskite photocathode and a perovskite/Si photovoltaic cell affords remarkable STH conversion efficiencies of 6.75% and 9.02%, respectively. The high-performance tandem devices demonstrate the prospective potential of organic-inorganic hybrid photoanodes for unassisted solar hydrogen production.
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Conformal heterojunction of a competent hole transport layer onto the nanoporous BiVO₄ photoanode is highly challenging despite its promise for unbiased photoelectrochemical (PEC) water splitting. Here, we grow a nanoscale conjugated polycarbazole framework (CPF-TCB) on nanoporous Mo:BiVO₄, and exhaustively assess its hole extraction capability. Type II band alignment in the CPF-TCB/Mo:BiVO₄ heterostructure enables the effective hole transport by suppressing charge recombination, enhancing both the fill factor and stability of the photoanode after loading a cocatalyst. The NiFeCoOₓ/CPF-TCB/Mo:BiVO₄ photoanode generates a superlative water oxidation photocurrent density of 6.66 mA cm⁻² at 1.23 V versus the reversible hydrogen electrode. By combining the photoanode with a perovskite photocathode and a perovskite/Si solar cell, two types of PEC tandem devices exhibit solar-to-hydrogen conversion efficiencies of 6.75% and 9.02%, respectively, which are the topmost records under tandem illumination mode. This work arranges a significant step for designing high-performance organic-inorganic hybrid photoelectrodes for solar hydrogen production.

Broader context
Photoelectrochemical (PEC) water splitting is a promising technology to produce green hydrogen without a carbon footprint. High solar-to-hydrogen (STH) conversion efficiency and long-term stability of tandem devices must be secured for the commercialization of the PEC approach. Bismuth vanadate (BiVO₄), providing a large photovoltage, has been considered an excellent photoanode material for tandem devices, but the nanostructuring and hole transport layers (HTL) are inevitable to overcome its charge recombination issue. However, it is very challenging not only to explore the HTL material with suitable band structures for BiVO₄ but also to uniformly coat it on the nanostructure. Here, we demonstrate a conjugated polycarbazole framework (CPF-TCB) as a new hole extraction layer for the nanoporous molybdenum-doped BiVO₄ photoanode for unassisted solar hydrogen production. Intimately contacted CPF-TCB/Mo:BiVO₄ heterostructure forms type II band alignment reinforcing charge separation. After loading a cocatalyst, the NiFeCoOₓ/CPF-TCB/Mo:BiVO₄ photoanode combined with a perovskite photocathode and a perovskite/Si photovoltaic cell affords remarkable STH conversion efficiencies of 6.75% and 9.02%, respectively. The high-performance tandem devices demonstrate the prospective potential of organic-inorganic hybrid photoanodes for unassisted solar hydrogen production.

Introduction
Photoelectrocatalysis, which is more efficient than photosvoltaic-electrocatalysis in the manufacturing process and photocatalysis in yield, is highly promising for solar hydrogen production.¹–³ The trade-off between photovoltage and photocurrent according to the band gap of a single photoelectrode requires an electrical bias to exceed water splitting voltage, which is a challenge in the photoelectrochemical (PEC) approach.⁴ For its ultimate goal, unassisted water splitting, tandem devices comprising dual light absorbers have been attempted to maximize photovoltage via light harvesting.⁵ In terms of the solar-to-hydrogen (STH) conversion efficiency for the tandem device, bismuth vanadate (BiVO₄) is an essential photoanode material owing to its suitable band gap enabling both high photovoltage and absorption spectrum separation with posterior absorber materials.⁶ Nevertheless, the short carrier diffusion length (~70 nm) incurs charge recombination,⁷ limiting its photocurrent density far below the theoretical value of 7.5 mA cm⁻².⁸

In addition to the nanostructuring of BiVO₄ itself to reduce the diffusion path, it is necessary to introduce charge transport layers to reinforce the charge separation.⁹ Specifically, since the hole transport is more susceptible to block by potential barriers along the carrier passage, it is inevitable to develop a competent hole transport layer (HTL) to improve the fill factor (FF) of BiVO₄ in order to secure high operating points of tandem devices. Unlike the various metal oxides, such as SnO₂,WO₃,TiO₂, and In₂O₃ that plainly construct type II band alignments favorable to electron transport under BiVO₄, the inorganic material d for HTL is highly limited. Due to its stringent requirements such as a low band gap, high durability, and more negative conduction band
edge than that of BiVO₄ only a few types of research on HTL have been reported. Quantum dot synthesis of carbon and black phosphorous elemental doping for carbon nitride has been attempted to form staggered band edges onto BiVO₄. Although these 2-step approaches of the coating after phase formation are advantageous for ensuring conductivity, possible degeneration in PEC performances by clogging the pores of nanostructured BiVO₄ or blocking the light also exists.

Conjugated polymers have been widely investigated in organic photovoltaics and perovskite solar cells. Their fascinating natures of tailored band structures stem from the diversity of functional groups. In addition, high electrical conductivity is retained without post-processing since π-electrons delocalized by alternating single bonds and double bonds facilitate the charge flows. These delocalized electrons in the π-conjugated backbone also contribute to electrochemical stability by preventing charge accumulation. Despite these favorable features for HTL, few studies have applied to nanostructured photoelectrodes owing to the difficulty of their direct growth without reducing specific surface area. Forming a heterojunction between nanoporous BiVO₄ and conjugated polymers with optimal band structures through conformal growth provides a breakthrough to the chronic issues in the efficiency and durability of photoanodes.

Here, we demonstrate the hole extraction of a conjugated polycarbazole framework (CPF-TCB) layer on the nanoporous molybdenum-doped BiVO₄ (Mo:BiVO₄) photoanode. Electropolymerization is utilized to conformally deposit CPF-TCB on Mo:BiVO₄ by elaborately controlling growth via a sweep cycle, and their uniform thickness is identified by transmission electron microscopy (TEM). After coating a tannic acid-based NiFeCoOₓ cocatalyst, the NiFeCoOₓ/CPF-TCB/Mo:BiVO₄ photoanode exhibits exceptional PEC water oxidation with a high photocurrent density of 6.66 mA cm⁻² at 1.23 V versus a reversible hydrogen electrode (V_RHE). X-ray spectroscopic analyses reveal the electronic environment of CPF-TCB/Mo:BiVO₄ and density functional theory (DFT) calculations suggest a theoretical basis for the charge transport within the heterojunction. Systematic studies about charge carrier dynamics verify the hole transport capability of CPF-TCB and confirm that the enhanced PEC performances originate from the type II band structures. For unbiased solar hydrogen production, two types of PEC tandem devices using the NiFeCoOₓ/CPF-TCB/Mo:BiVO₄ photoanode with a perovskite photocathode and a perovskite/Si electron transport layer (ETL) under the photoanode.

Results and discussion

The fabrication processes of photoanodes are schematically illustrated in Fig. 1S (ESI†). All designs of the photoanode were carried out with a focus on efficiently separating and transferring charges generated in BiVO₄. Firstly, BiVO₄ was synthesized from electrodeposited BiOI nanoplates as a precursor to possess nanopores, providing a large specific surface area and short diffusion path. During the annealing process, the removal of surface trap sites in BiVO₄ was induced by the molybdenum doping. For maximization of surface area and electron extraction, vertical nanorod-type SnO₂ was introduced as an electron transport layer (ETL) under the photoanode. The thin CPF-TCB layer was directly synthesized onto the surface of Mo:BiVO₄ using electropolymerization, and the CPF-TCB/Mo:BiVO₄ photoanode was dip-coated with tannic acid-based NiFeCoOₓ acting as a cocatalyst. Conformal coating of conductive polymers on BiVO₄ without filling its nanopores is highly challenging. As illustrated in Fig. 1(a), the electropolymerization we adopted is sophisticated in that the monomers can intimately contact all surfaces of the photoanode. As a building block to construct the conjugated polycarbazole framework, we employed 1,3,5-Tris(N-carbazolyl)benzene (TCB) which contains carbazole. Among various aromatic units, such as benzene, thiophene, and pyridine, carbazole applied in the conjugated polymer backbone contributes to the electrochemical stability because of its electrophilic substitution in the nitrogen atom and the aromatic ring. The CPF-TCB films were electropolymerized on the Mo:BiVO₄ photoanode by the linear sweep voltammetry and their thickness was controlled by the sweep cycle. In current density-potential (J-V) curves (Fig. S2 (ESI†)), increases in current density were observed around 1.2 V as the sweep number increased. This indicates that as the monomers polymerized, the formed larger frameworks increased the number of sites where additional monomers could attach. We observed bright yellowish Mo:BiVO₄ surfaces became cloudy after polymerization and also checked a color change to yellow when coated on the fluorine-doped tin oxide (FTO), as shown in Fig. S3 (ESI†).

The X-ray diffraction (XRD) patterns in Fig. 1(b) were indexed to monoclinic BiVO₄ (PDF# 04-010-5173), showing that the crystal structure of BiVO₄ was unchanged after deposition of the CPF-TCB. In the top field-emission scanning electron microscopy (FESEM) image of CPF-TCB/Mo:BiVO₄ (Fig. 1(c)), the coexistence of nanopores and ETL-derived mesopores was observed, leading to the maximized surface area of the photoanode. The overall morphology of the 2.5 μm-thick vertical photoanode suitable for light absorption was confirmed through the cross-sectional FESEM image (Fig. 1(d)). Since the CPF-TCB thin layer with optimal sweep cycle was indistinguishable, we prepared Mo:BiVO₄ with 40 time-swept CPF-TCB. As exhibited in Fig. S4 (ESI†), even at high cycles, the CPF-TCB layer was uniformly coated on Mo:BiVO₄ without agglomeration and clogging of nanopores. Corresponding energy dispersive X-ray (EDX) mapping indicated the uniform distribution of C and N elements from CPF-TCB on the BiVO₄ surface. The CPF-TCB film with the optimal sweep cycle was revealed in the TEM image. As shown in Fig. 1(e), the CPF-TCB thin layer was conformally covered around the Mo:BiVO₄. High-resolution TEM (HRTEM) image (Fig. 1(f)) exposed that under the optimal sweep cycle, the CPF-TCB grew uniformly onto Mo:BiVO₄ with a thickness of 5 nm. The
amorphous nature of the CPF-TCB was consistent with the characteristics of electropolymerized polycarbazole frameworks in previous studies, also corresponding to XRD results showing no difference before and after deposition (Fig. 1(b)). The lattice fringes with interplanar spacings of 2.57 and 2.63 \( \text{Å} \) in two directions correspond to (020) and (200) planes, respectively. The fast Fourier transformation (FFT) patterns in Fig. 1(g) show the diffraction spots for (200) and (020) planes, indicating the crystalline monoclinic phase (12/b group). These results well matched with the XRD analysis, identifying the suitable phase for water oxidation.

The photoelectrochemical water oxidation of the fabricated photoanodes was evaluated in a three-electrode cell with 1 M potassium borate (K-B) buffer (pH 9.5) under AM1.5G solar illumination. To investigate the optimal thickness of the CPF-TCB layer for Mo:BiVO$_4$, the electropolymerizations of CPF-TCB were executed with different sweep cycles (5, 10, and 20 cycles). In \( J-V \) curves of the CPF-TCB/Mo:BiVO$_4$ photoanodes (Fig. S5 (ESI†)), they exhibited similar photocurrent densities at 1.23 \( \text{V}_{\text{RHE}} \) whereas CPF-TCB with 10 cycles made the largest polarization. This indicates effective charge separation, and it was confirmed to grow a thickness of 5 nm under 10 cycles (Fig. 1(f)). The PEC characteristics of Mo:BiVO$_4$ before and after the 10-cycle deposition of the CPF-TCB layer were evaluated with and without the NiFeCoO$_4$ cocatalyst. The \( J-V \) curves for four types of photoanodes are presented in Fig. 2(a). The photocurrent density of CPF-TCB/Mo:BiVO$_4$ was measured to 3.82 mA cm$^{-2}$ at 1.23 \( \text{V}_{\text{RHE}} \), which is higher than that of Mo:BiVO$_4$ (3.30 mA cm$^{-2}$). Since the improvement was more pronounced with the cocatalyst, NiFeCoO$_4$/CPF-TCB/Mo:BiVO$_4$ reached a remarkable
The photoelectric current density of 6.66 mA cm$^{-2}$ at 1.23 V$_{\text{RHE}}$, which is higher than that of NiFeCoO$_x$/Mo:BIVO$_x$ (6.09 mA cm$^{-2}$). It means that CPF-TCB contributes to effective hole transport from Mo:BIVO$_x$ to the cocatalyst. To verify the exceptional photoelectric current density, linear sweep voltammetry (LSV) of five NiFeCoO$_x$/CPF-TCB/Mo:BIVO$_x$ photoanodes fabricated by the same process were conducted. Fig. S6 (ESH) shows a minor variation in PEC performances between samples, indicating that the NiFeCoO$_x$/CPF-TCB/Mo:BIVO$_x$ photoanode has good reproducibility. As shown in SEM images of NiFeCoO$_x$/CPF-TCB/Mo:BIVO$_x$ (Fig. S7 (ESH)), no structural changes were observed in the photoanode before and after the LSV measurement, indicating that the CPF-TCB and NiFeCoO$_x$ effectively protect Mo:BIVO$_x$ and promote water oxidation. The resulting significant enhancement in 0.4 ~ 0.8 V$_{\text{RHE}}$ is advantageous to provide high power at the general range of the operating point in PEC tandem devices. The contribution of CPF-TCB to the power of the photoanode was quantitatively evaluated by the fill factor, as shown in Fig. 2(b). It is noteworthy that the maximum power point with the CPF-TCB layer was achieved at a more cathodic potential of 0.65 V$_{\text{RHE}}$ compared to that without the layer (0.75 V$_{\text{RHE}}$), indicating that CPF-TCB served to elevate both photocurrent and photovoltage. Based on the rectangularity at the maximum power point, we calculated the FF of the photoanodes using the following equation:

$$FF(\%) = \frac{\text{J}_{\text{MP}}(1.23 - V_{\text{MP}})}{\text{J}_{\text{MP}}(1.23 - V_{\text{OC}})}$$

where the $J_{\text{MP}}$ and $V_{\text{MP}}$ are the current density and potential at the maximum power point, $J_{\text{OC}}$ is the current density at 1.23 V$_{\text{RHE}}$, and $V_{\text{OC}}$ is the onset potential. When the CPF-TCB layer was inserted between NiFeCoO$_x$ and Mo:BIVO$_x$, the FF increased from 32.57 to 40.59%. The improvement in power efficiency makes application to PEC tandem devices more advantageous. The photocurrents of photoanodes were also verified by the incident photon-to-current conversion efficiency (IPCE) measured at 1.23 V$_{\text{RHE}}$. In photoanodes containing CPF-TCB, the increases in IPCE were confirmed in the wavelength range below 500 nm regardless of the presence of the cocatalyst. Especially, the maximum value of NiFeCoO$_x$/CPF-TCB/Mo:BIVO$_x$ was improved by 10% compared to NiFeCoO$_x$/Mo:BIVO$_x$ achieving near-complete IPCE near 450 nm. The IPCE spectra were integrated with photon flux over wavelength to revalidate the current density. The integrated photocurrent densities of all four types of photoanode practically matched the current density in J-V curves (Fig. 2(a)).

The hole extraction ability of CPF-TCB was further proven by the electrochemical impedance spectroscopy (EIS) conducted at 0.5 V$_{\text{RHE}}$, where large photocurrent differences appeared. The Nyquist plots were fitted with an equivalent circuit suggested in Fig. 2(d), and their values were tabulated in Table S1 (ESH). The charge transfer resistance ($R_\text{ct}$) of NiFeCoO$_x$/CPF-TCB/Mo:BIVO$_x$ (41.45 Ω cm$^2$) was similar to that of NiFeCoO$_x$/Mo:BIVO$_x$ (42.65 Ω cm$^2$), showing the same charge injection of the cocatalyst. For the charge transport resistance ($R_\text{ct}$) in photoanode, NiFeCoO$_x$/CPF-TCB/Mo:BIVO$_x$ had a lower value of 5.525 Ω cm$^2$ compared to NiFeCoO$_x$/Mo:BIVO$_x$ (36.13 Ω cm$^2$). The significant decrease in $R_\text{ct}$ indicates that the enhancement of PEC performance sprang from
the hole extraction behavior of CPF-TCB. The durability of photoanodes was examined by the chronoamperometry at 1.23 V_{BCE}. As shown in current density-time (I-t) curves (Fig. 2(e)), the NiFeCoO_{x}/CPF-TCB/MoBiVO_{x} photoanode ran stably for 5 h, whereas the NiFeCoO_{x}/MoBiVO_{x} photoanode exhibited a sharp degradation within 1 h. It means the role of CPF-TCB includes the protective layer as well as the HTL for MoBiVO_{x}. The improved stability is also indirect evidence of the efficient hole extraction of CPF-TCB. The instability of the photoanode is derived from the hole accumulation causing self-oxidation of BiVO_{x}. The expedited charge separation by CPF-TCB prevents the hole accumulation, enhancing the PEC stability. Furthermore, gas chromatography was conducted to collect the evolved gas and measure the Faradaic efficiency. As shown in Fig. 2(f), Faradaic efficiencies of nearly 100% were acquired in both the NiFeCoO_{x}/CPF-TCB/MoBiVO_{x} photoanode and Pt cathode, presenting that generated charges were fully consumed for oxygen and hydrogen evolution. It was also confirmed that the actual gas evolution rates were close to the calculated values.

The formation of the CPF-TCB layer was further proved by Fourier transform-infrared (FT-IR) spectroscopy, as shown in Fig. 3(a). Within the wavenumber range of 1000 to 1800 cm^{-1} where typical polymer bonding is observed, no peaks were observed for MoBiVO_{x}. On the other hand, several peaks were identified in CPF-TCB/MoBiVO_{x}, among which peaks at 1223, 1329, 1438, 1462, and 1591 cm^{-1} were found to originate from the carbazole functional group in CPF-TCB. These spectra most directly verify that the amorphous CPF-TCB thin film was well formed on MoBiVO_{x}. To further demonstrate the charge transport behavior of CPF-TCB and the resulting changes in the electronic states of MoBiVO_{x}, X-ray absorption spectroscopy (XAS) was employed for the V K-edge of MoBiVO_{x} with and without CPF-TCB. In the Fourier-transformed extended X-ray absorption fine structure (EXAFS) spectra (Fig. 3(b)), the peak corresponding to V-O bonding was observed around 1.3 Å for both samples, confirming that CPF-TCB had no influence on the interatomic structure of MoBiVO_{x}. X-ray absorption near edge structure (XANES) spectra for the V K-edge in Fig. 3(b) show the electronic state changes. After forming the CPF-TCB layer on MoBiVO_{x}, the pre-edge peak shifted from 5469.4 to 5469.8 eV, and the edge peak shifted from 5501.4 to 5502.6 eV. The prominent shifts imply the relative electron transport towards MoBiVO_{x} due to charge separation caused by hole extraction of CPF-TCB.\(^2^6\)

![Fig. 3 Spectroscopic analyses of conjugated polycarbazole frameworks.](image)

(a) FT-IR spectra of MoBiVO_{x} and CPF-TCB/MoBiVO_{x}. (b) V K-edge XANES spectra of MoBiVO_{x} and CPF-TCB/MoBiVO_{x}. (c) V 2p XPS spectra of MoBiVO_{x} and CPF-TCB/MoBiVO_{x} with different Ar plasma etching times. (d) N 1s XPS spectra of CPF-TCB and CPF-TCB/MoBiVO_{x} with different Ar plasma etching times.
X-ray photoelectron spectroscopy (XPS) analysis of Mo:BiVO₄, CPF-TCB, and their heterojunction was carried out to scrutinize the electronic structures, and wide spectra were presented in Fig. S9 (ESI†). As shown in Fig. 3(c), after the deposition of CPF-TCB, the V 2p₁/₂ and 2p₃/₂ peaks shifted from 523.53 and 516.13 eV to the higher binding energies of 523.86 and 516.56 eV, respectively. The Bi 4f₁/₂ and 4f₃/₂ peaks also shifted from 163.83 and 158.53 eV to the higher binding energies of 164.16 and 158.86 eV, respectively (Fig. S10 (ESI†)). In contrast, the N 1s peak (400.20 eV) in carbazole slightly moved to the lower binding energy of 400.16 eV, as exhibited in Fig. 3(d). These tendencies in bin ding energy are attributed to the strong interfacial interactions between CPF-TCB and Mo:BiVO₄.²⁷,²⁸ Depth profiling was performed while etching the surface of CPF-TCB/Mo:BiVO₄ by irradiating Ar plasma with time variation. The N 1s peak intensity gradually decreased over time and completely disappeared after 10 min plasma, indicating that the 5 nm-thick CPF-TCB layer was etched in 10 min. On the other hand, the V 2p peak intensity remained constant after a slight decrease over time, and the Bi 4f peaks maintained high intensity regardless of time. The transition of peak positions during etching was ascribed to the change in the interaction between CPF-TCB and Mo:BiVO₄. Meanwhile, the final NiFeCoO₄/CPF-TCB/Mo:BiVO₄ photoanode was also analyzed by XPS, as shown in Fig. S11 (ESI†). The compositional elements of the cocatalysts were revealed in Ni 2p (873.3 and 855.6 eV for 2p₁/₂ and 2p₃/₂), Fe 2p (724.3 and 710.9 eV for 2p₁/₂ and 2p₃/₂), and Co 2p (796.5 and 781.8 eV for 2p₁/₂ and 2p₃/₂) spectra. C 1s peak was deconvoluted into three peaks presenting C=O (288.6 eV), C–O (285.5 eV), and C=C (284.5 eV) bonds, which were derived from the tannic acid chelating metal ions.²⁹ Metal-hydroxide bonds (M–O and M–OH) that appeared in deconvoluted O 1s peaks were also attributed to the photocatalyst.³⁰

To theoretically scrutinize the charge transport behavior within the CPF-TCB/Mo:BiVO₄ heterostructure, the DFT calculations were utilized. As suggested in Fig. S12 (ESI†), a single layer of CPF-TCB positioned on the (010) surface of BiVO₄ was established as the DFT calculation model to elucidate the spatial distribution of charge density differences. Fig. 4(a) shows the 3-dimensional charge density difference across the CPF-TCB/Mo:BiVO₄ interface. The charge redistribution mainly occurred at the interface of the CPF-TCB/Mo:BiVO₄, and electrons accumulated around the surface of Mo:BiVO₄. It is one piece of evidence indicating favorable charge transport at the interface of the heterostructure, which is consistent with the aforementioned results of XAS and XPS analysis.²³,²⁴ Additionally, the planar-averaged charge density difference along the z-direction normalized to the CPF-TCB/Mo:BiVO₄ heterostructure was calculated to investigate quantitative changes (Fig. 4(b)). Strong charge accumulation on the surface of Mo:BiVO₄ indicates that electrons mainly transport from CPF-TCB to Mo:BiVO₄ at their interface. According to Bader charge analysis, about 0.05 electrons per supercell are transported from the CPF-TCB layer to Mo:BiVO₄ (010). After reaching the equilibrium state, a built-in electric field is developed by the net charge accumulation across the CPF-TCB/BiVO₄ heterostructure, promoting charge separation.³² Thereby, these calculations provide support for the crucial charge transport role of CPF-TCB exposed in PEC measurements.

The hole extraction capability of CPF-TCB was further demonstrated by Mott-Schottky (M-S) analysis under light-off. Comparing the M-S plots shown in Fig. 5(a), the flat band potentials of TCB/Mo:BiVO₄ and Mo:BiVO₄ were almost identical. It was in line with the J-V curves in Fig. 2(a), where there was no difference in the onset potential of the two photoanodes. However, the slope of CPF-TCB/Mo:BiVO₄ was lower than that of Mo:BiVO₄, indicating that the donor density (N_d) of Mo:BiVO₄ rises when it forms a heterojunction with CPF-TCB. The donor density was calculated by the following equation and tabulated in Table S2 (ESI†):

\[ C^{-2} = \frac{2}{\varepsilon_0 A_{Fe} N_d}[V - E_B - (k_BT)/e] \]

where \( C \) is the capacitance of the space charge layer (F), \( \varepsilon \) is dielectric constant (~68), \( \varepsilon_0 \) is the permittivity of vacuum (8.854 × 10⁻¹² F m⁻¹), \( A \) is the surface area (m²), \( e \) is the electron charge (1.602 × 10⁻¹⁹ C), \( V \) is the applied potential (V), \( E_B \) is the flat band potential (V), \( k_B \) is the Boltzmann constant (1.381 × 10⁻²³ J K⁻¹), and \( T \) is the temperature (298 K). The higher donor density of CPF-TCB/Mo:BiVO₄ (2.125 × 10²⁰ cm⁻³) than that of Mo:BiVO₄ (1.438 × 10²⁰ cm⁻³) represents that CPF-TCB enhanced charge separation as the HTL. The open circuit potential (OCP) transient decay profile is a powerful tool providing information about the behavior of charges induced by photovoltage.²⁵ As shown in normalized OCP profiles (Fig. S13 (ESI†)), the CPF-TCB/Mo:BiVO₄ photoanode exhibited faster decay than Mo:BiVO₄ under light-off. The faster decay profile is caused by the rapid relaxation of charge carriers in the elimination of the illumination, conversely indicating the boosted charge separation under illumination. The carrier lifetime (\( \tau_c \)) was quantified by the following equation:

\[ \tau_c = \frac{1}{(dOCP/dt)} \]

where \( \tau_c \) is the time derivative of the OCP transient decay. As presented in Fig. 5(b), the carrier lifetime of CPF-TCB/Mo:BiVO₄ is 2.18 ms, which is shorter compared to 6.18 ms for Mo:BiVO₄. The faster decay time is indicative of the larger charge recombination after light-off, implying the expedited charge separation of the heterojunction under illumination.³³,³⁵

To make a comparison of the charge recombination behavior in two BiVO₄-based photoanodes, the photoluminescence (PL)
analysis was executed. Fig. 5(c) shows the steady-state PL spectra of MoBiVO₄ with and without CPF-TCB, displaying peaks at 550 nm originating from radiative charge recombination. The PL emission was intensively quenched in forming CPF-TCB/MoBiVO₄ heterojunction, meaning that the HTL suppressed the intrinsic radiative recombination of charges in MoBiVO₄. The benefit of the heterojunction was further supported by time-resolved photoluminescence (TRPL) elucidating the charge carrier kinetics (Fig. 5(d)). The decay obtained at the PL peak of 550 nm was fitted by the biexponential decay model as below, offering two carrier lifetimes ($\tau_1$ and $\tau_2$).

$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$$

where $I$ and $A$ are intensity and amplitude, respectively. As tabulated in Table S3 (ESI†), the $\tau_2$ values associated with non-radiative decay caused by trap sites were similar (0.2058 ns and 0.1455 ns). However, the radiative recombination-related $\tau_1$ of CPF-TCB/MoBiVO₄ (1.750 ns) was shorter than that of MoBiVO₄ (3.899 ns). The average carrier lifetime ($\tau_{avg}$) also decreased from 1.830 to 0.6740 ns after depositing CPF-TCB. These lifetime drops denote the expedient extraction of photoexcited holes by CPF-TCB as a hole transport layer. The fundamental cause of effective charge separation in CPF-TCB/MoBiVO₄ was disclosed in the band structure analysis. Ultraviolet-visible (UV-vis) spectroscopy was measured, and the absorption spectra calculated by the measured transmittance and reflectance were converted to Tauc plots, as shown in Fig. S14 (ESI†). The optical band gaps of MoBiVO₄ and CPF-TCB were 2.44 and 3.26 eV, respectively. Ultraviolet photoelectron spectroscopy (UPS) was utilized to precisely determine the work functions and band edge positions, as suggested in Fig. S15 (ESI†). The secondary electron emission (SEE) spectra exposed the work function of MoBiVO₄ (4.25 eV) and CPF-TCB (4.11 eV) from the difference with the source energy. From the valence band (VB) spectra in the low binding energy region, the energy differences between the Fermi level and VB maximum were verified. The band structure of CPF-TCB/MoBiVO₄ was constructed by
combining UV-vis spectra and UPS, as illustrated in Fig. 5(e). The CPF-TCB formed a type II heterojunction with MoBIVO₄. This band alignment is energetically favorable for not only the efficient extraction of photogenerated holes but also the block of photogenerated electrons in MoBIVO₄, reinforcing the charge separation. As a result, the aforementioned characteristics of CPF-TCB/MoBIVO₄, such as induced charge recombination, rapid hole extraction, and resulting increased carrier concentration, all stem from the band structure.

To implement unbiased solar hydrogen production, the ultimate goal of PEC water splitting, we fabricated two types of tandem devices using the final NiFeCo₂O₄/CPF-TCB/MoBIVO₄ photoanode. The key requirement for the bottom cell is to avoid overlapping absorption of the photoanode to generate high photocurrent through light harvesting while being able to generate sufficient photovoltage. Thus, for optimal band gap matching with 2.44 eV of MoBIVO₄, halide perovskite-based bottom cells were prepared. Firstly, a perovskite-photocathode (PA-PC) tandem device was fabricated by combining the NiFeCo₂O₄/CPF-TCB/MoBIVO₄ PA and the perovskite PC. The photocathode illustrated in Fig. S16 (ESI†) exhibited prominent PEC performances (photocurrent density of 19.0 mA cm⁻² at 0 V_RHE and onset potential of 1.03 V_RHE in potassium phosphate (K₃PO₄) buffer). As shown in Fig. 6(a), the PA-PC tandem device was measured in the K-B buffer under tandem illumination mode. The operating current density (J_0) determined by the intersection of 3 electrode J-V curves of the PA and PC behind it was 5.49 mA cm⁻² at 0.81 V_RHE, which corresponded to a STH conversion efficiency of 6.75%. Secondly, a photovoltaic-photocathode (PV-PA) tandem device was fabricated by combining the PA and the perovskite/Si solar cell. As displayed in Fig. S17 (ESI†), the PV cell made a similar current density (short-circuit current density of 19.2 mA cm⁻²) but higher voltages (open-circuit voltage of 1.81 V) compared to photocathodes, since Si generated additional photovoltage by absorbing light transmitted from perovskite. The higher photovoltage allowed the operating point of the PV-PA tandem device to be formed at a higher voltage, delivering a higher J_0. Fig. 6(b) shows the 2-electrode J-V curves of the PEC cell comprising a Pt cathode and the NiFeCo₂O₄/CPF-TCB/MoBIVO₄ PA and the PV cell behind it under mode T. The J_0 of the PV-PA tandem device was 7.33 mA cm⁻² at 1.30 V, which corresponded to a STH conversion efficiency of 9.02%.

Finally, two fabricated tandem devices were measured by chronocoulometry without external bias under mode T (Fig. S18 (ESI†)). As shown in the J-t curve (Fig. 6(c)), the PA-PC tandem device recorded the current density consistent with the
and the corresponding STH conversion efficiency, durably operating for 10 h. Also, the PV-PA tandem device was stably operated for 10 h, generating the current density in accordance with \( J_{\text{FP}} \) and STH conversion efficiency of 9% (Fig. 6(d)). The PA-PC and PV-PA tandem device we implemented shows the best STH conversion efficiency among each type of tandem devices with BiVO\(_4\)-based photoanodes, as shown in Fig. 6(e). Moreover, it is noteworthy that both types recorded the highest STH conversion efficiency among the mode T tandem devices, which require systematic engineering for the separation of absorption wavelength (Tables S4 and S5 [ESI]). These results emanate from the high-efficiency tandem device-tailored photoanode, in which a remarkable HTL, CPF-TCB, simultaneously increases the photocurrent and photovoltage of Mo:BiVO\(_4\).

Conclusion

We have successfully expedited the hole transport of the nanoporous Mo:BiVO\(_4\) photoanode by harnessing a CPF-TCB layer via electropolymerization, where the sophisticated control enabled the direct and conformal growth of CPF-TCB without plugging nanopores. Effective charge transport in CPF-TCB/Mo:BiVO\(_4\) heterojunction was disclosed by XANES and XPS analyses, and depth profiling reaffirmed the heterostructure. The planar-averaged charge density difference by the DFT calculations substantiated strong charge separation in CPF-TCB/Mo:BiVO\(_4\). Based on the investigation of charge carrier dynamics, we proved that enhanced hole transport through the CPF-TCB layer suppressed charge recombination and elevated the charge density of the photoanode. Consequently, the NiFeCoO\(_x\)/CPF-TCB/Mo:BiVO\(_4\) photoanode generated an outstanding water oxidation photocurrent density of 6.66 mA cm\(^{-2}\) at 1.23 V\(_{\text{BEG}}\). Also, its high fill factor played a key role in both types of tandem devices for unassisted solar hydrogen production. The PA-PC tandem device combined with the perovskite photocathode and PV-PA tandem device assembled with perovskite/Si solar cell recorded STH conversion efficiencies of 6.75% and 9.02%, respectively, which are the topmost records among not only BiVO\(_4\)-based but also mode T tandem devices. This work broadens the material pool and provides novel strategies for designing high-performance organic-inorganic hybrid photoelectrodes for solar hydrogen production.

Experimental section

Synthesis of nanoporous Mo:BiVO\(_4\) photoanodes

SnO\(_2\) NRs as an electron transport layer were fabricated by e-beam evaporation on the FTO glasses with a size of 1 x 1.5 cm\(^2\). After depositing a 50 nm-thick SnO\(_2\) film as an adhesive layer, 2.5 \( \mu \text{m} \)-thick SnO\(_2\) NRs were formed with a glancing angle of 85° and a rotation of 80 rpm. Nanoporous Mo:BiVO\(_4\) was prepared by the modified two-step electrodeposition on the SnO\(_2\) NRs annealed at 550 °C for 2 h in the air.\(^{9,15}\) The 50 mL aqueous solution with pH 1.8 contained 0.4 M KI (Daejung, 99.5%), 15 mM Bi(NO\(_3\))\(_2\)-5H\(_2\)O (Junsei, 98%), and 30 mM lactic acid (Sigma-Aldrich, 85%). The 20 mL of ethanol (Daejung, 99.9%) dissolved 46 mM p-benzoquinone (Junsei, 98%) was slowly mixed with the as-prepared solution. After cooling the solution temperature to 22 °C, BiO\(_2\) was electrodeposited in the three-electrode cell with Ag/AgCl electrode and Pt mesh. Nucleation of BiO\(_2\) with a potential -0.35 V\(_{\text{Ag/AgCl}}\) for 20 s was followed by its growth with a potential -0.1 V\(_{\text{Ag/AgCl}}\) for 4 min. The 10 μL aqueous solution with 0.1 M Na\(_2\)MoO\(_4\) (Sigma-Aldrich, 98%) was added into 5 mL dimethyl sulfoxide (DMSO) (Kanto, 98%) dissolved 0.2 M VO(acac)\(_2\) (Sigma-Aldrich, 98%). As-deposited BiO\(_2\) was converted to Mo:BiVO\(_4\) by annealing at 450 °C for 2 h in the air after impregnating the solution. The excess V\(_2\)O\(_5\) was removed from the Mo:BiVO\(_4\) photoanode by immersing it in 1 M NaOH solution (Daejung) for 10 min.

Surface modification with CPF-TCB hole transport layers and NiFeCoO\(_x\) cocatalysts

The CPF-TCB films were fabricated by electropolymerization on Mo:BiVO\(_4\) photoanodes. The mixed solvent with 28 mL acetonitrile (Daejung, 97.9%) and 42 mL dichloromethane (Daejung, 99.5%) obtained a conductivity by dissolving 0.1 M tetrabutyliammonium perchlorate (Sigma-Aldrich, 95%). The 4 mM 1,3,5-Tris(N-carbazolyl)benzene (Sigma-Aldrich, 97%) was dissolved in the solution for 10 min. The potential of Mo:BiVO\(_4\) photoanode was linearly swept in the range of -0.8 ~ 1.4 V\(_{\text{Ag/AgCl}}\) with a scan rate of 20 mV s\(^{-1}\). After electropolymerization, the photoanode was rinsed with acetonitrile and ethanol, followed by drying with \( \text{N}_2\) flow. The NiFeCoO\(_x\) cocatalysts were introduced by the dip coating modified from previous methods.\(^{12}\) The 2 mL of 10 mM FeCl\(_3\)-6H\(_2\)O (Daejung, 98%), 7 mL of 10 mM NiCl\(_2\)-6H\(_2\)O (Daejung, 96%), and 1 mL of 10 mM CoCl\(_2\)-6H\(_2\)O (Daejung, 97%) solutions were mixed in a vessel. After immersing the CPF-TCB/Mo:BiVO\(_4\) photoanode in the vessel for 15 min, the 10 mL of 9 mg L\(^{-1}\) tannic acid (Sigma-Aldrich) solution and the 75 μl of 2 M NaOH (Daejung, 97%) solution were sequentially added. After 1 h, the photoanode was rinsed with deionized water and dried with \( \text{N}_2\) flow.

Fabrication of the perovskite photocathodes

The FTO glass was patterned by a laser-etching instrument (Korthem Science), followed by UV treatment for 15 min. As an ETL, the SnO\(_2\) colloidal dispersion (Alfa Aesar) with deionized water (1:4; volume ratio) was spin-coated at 3000 rpm for 60 s and heated at 170 °C for 1 h. The perovskite solution was prepared by dissolving 240.8 mg of FAI (Greatcell Solar, 99.999%), 8.25 mg of MABr (Greatcell Solar, 99.999%), 33.76 mg of MACl (Greatcell Solar, 99.999%), 18.19 mg of CaI (Sigma-Aldrich, 99.999%), 705.3 mg of PbI\(_2\) (Sigma-Aldrich, 99.999%), and 27.04 mg of PbBr\(_2\) (Sigma-Aldrich, 99.999%) in 0.96 mL of DMF (Sigma-Aldrich, 99.8%) and 0.24 mL DMSO (Sigma-Aldrich, 99.9%) mixed solvent. Subsequently, the solution was stirred for 1 h in an ambient air atmosphere. The perovskite solution was spin-coated at 1200 rpm for 12 s and 5800 rpm for 20 s, followed by annealing at 100 °C for 1 h. An anti-solvent, ethyl acetate (0.8 mL), was dripped onto the substrate 10 s before the end of the spin-coating process. As an HTL, the spiro-OMeTAD solution comprising 72 mg
of spiro-OMeTAD (Sigma-Aldrich, 99%), 8.8 μL of Li-TFSI (Sigma-Aldrich, 99.99%) solution (520 mg of Li-TFSI in 1 mL of acetonitrile), and 4.4 μL of 4-tert-Butylpyridin (Sigma-Aldrich, 98%) was dissolved in 1 mL of chlorobenzene and spin-coated on the perovskite at 3000 rpm for 30 s. An 80 nm-thick Au top electrode was deposited on the HTL by thermal evaporation. Cu tape and wire were attached to the Au electrode, followed by sealing with an epoxy. Finally, the Pt cocatalyst was deposited on the active area by using a sputter coater (Cressington 108 Auto, Ted Pella).

Fabrication of the perovskite/Si solar cells

The perovskite/Si tandem solar cells were fabricated by the previously reported method. For a brief, on the top of the Si bottom cell with 20 nm-thick of indium tin oxide (ITO) recombination layer, 7 mg mL⁻¹ poly(triarylamine) (PTAA, Sigma-Aldrich) solution in toluene was spin-coated at 6000 rpm for 30 s and annealed at 100 °C for 10 min. The 1.3 M perovskite (Cs0.3DMA₂₂MA₃₃PbI₆) solution with 10 mol% of MAC (Lumtec, 99.5%), 1.5 mol% of PEASCN (Greatcell Solar), and 2 mol% of Pb(SCN)₂ additives in dimethylformamide (DMF, Sigma-Aldrich, 99.8%) and N-methyl-2-pyrrolidone (Sigma-Aldrich, 99%) mixed solvent (4:1; volume ratio) was spin-coated on PTAA at 3000 rpm and annealed at 100 °C for 10 min. On the perovskite layer, 15 nm-thick Cs₅₀ (Nano-C) layer was deposited by thermal evaporation, and 0.2 wt% polyethyleneimine (Sigma-Aldrich, 80% ethoxylated) solution in methanol was dynamically spin-coated at 6000 rpm for 30 s. A 40 nm-thick ITO layer was deposited by radio frequency sputtering at room temperature (base pressure: 2 × 10⁻⁶ Torr, working pressure: 2 × 10⁻³ Torr, Power: 50 W), and a 500 nm-thick, 50 μm-width Ag grid was deposited by thermal evaporation. Finally, a 105 nm-thick MgF₂ (Sigma-Aldrich, 99.99%) layer was deposited as an anti-reflection layer.

Characterizations

The crystal structures of the samples were identified using XRD (D8 Advance, Bruker) with Cu Kα (1.5406 Å) radiation. The surface morphology and EDX of the samples were investigated by FESEM (MERLIN Compact, ZEISS) with acceleration voltages of 5 and 15 kV, respectively. The HRTEM images and FFT patterns of CPF-TCB/Mo:BiVO₄ were analyzed by TEM (JEM-2100F, JEOL) with an acceleration voltage of 200 kV. FT-IR spectra were recorded with absorbances of FT-IR spectrometer ( Nicolet iS50, Thermo Fisher Scientific). The XAS data at V K-edge was fitted using Athena software (Demeter). The electronic states and spin density of the samples were identified using XPS (AXIS Nova, KRATOS). The current density was measured using a source meter (2400, Keithley) with the cathodic potential scan in a dark box.

Photoelectrochemical measurements

A Xe arc lamp (LS 150, Abet Technologies) was used as a light source. Its illumination and intensity were calibrated with AM1.5G filter and Si photodiode (S300, McScience), respectively. The PEC measurements were carried out using a potentiostat (Ivium-n-Stat, Ivium Technologies) in the three-electrode cell with the Ag/AgCl electrode and Pt mesh. Water oxidation of photoanodes was measured in 1 M K-B, buffer (pH 9.5), and proton reduction of perovskite photocathodes was measured in 0.5 M K-P, buffer (pH 7.0). All the measured potentials were converted into RHE by the Nernst equation:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E^{\circ}_{\text{Ag/AgCl}} + 0.059 \times \text{pH} \]

where, \( E_{\text{Ag/AgCl}} \) is the measured potential (V) versus the Ag/AgCl electrode, and \( E^{\circ}_{\text{Ag/AgCl}} \) is 0.198 V at 25 °C. For the J-V curves, the potential was swept toward the anodic direction with a scan rate of 20 mV s⁻¹ under chopped illumination. The IPCE was measured with separated light by a monochromator (MonoRά150i, Dongwoo Optron) at 1.23 V_RHE. The current density was calculated by integrating the spectral current density, obtained by multiplying the spectral photon flux by IPCE, over the wavelength. The EIS was recorded from 100 kHz to 1 Hz with an amplitude of 10 mV at 0.5 V_RHE. The EIS Nyquist plots were fitted with ZView software (Scribner Associates). The J-t curves were recorded at 1.23 V_RHE. The gas chromatography system (7890B, Agilent Technologies) was connected to an air-light H-cell with the photoanode and Pt mesh to calculate the Faradaic efficiencies and gas evolution rates at 1.23 V_RHE. The M-S plots were recorded at a frequency of 1 kHz with the cathodic potential scan in a dark box.

The donor densities were calculated by the slope of the plot. On the open circuit condition, the OCP of photoanodes was stabilized for 10 min under illumination, and the OCP decay was recorded for the next 10 min after light-off. The OCP-derived carrier lifetimes were calculated by differentiating the OCP with respect to time. The J-V curves of the perovskite photocathode were recorded behind the photoanode in the 3-electrode cell with Ag/AgCl electrode, Pt mesh, and 1 M K-B, buffer (pH 9.5). After combining the photoanode and photocathode, the J-t curve of the PA-FC tandem device was measured under the bias of 0 V. The J-V curves of the perovskite/Si solar cells were measured using the potentiostat (CHI 608C, CH Instruments) and the AAA-graded AM1.5G solar simulator (PEC-L11, Peccell Technologies) calibrated by standard Si cell with quartz filter (91150 V, Newport). The J-V curves of 2-electrode cell with the NiFeCoO₄/CPF-TCB/Mo:BiVO₄ photocathode and Pt cathode were recorded in 1 M K-B, buffer (pH 9.5), and those of solar cell were measured behind the photoanode. After connecting the bottom electrode of the solar cell to the photoanode and the top electrode.
to the cathode, the J-t curve of the PV-PA tandem device was measured under the bias of 0 V. The STH conversion efficiencies of tandem devices were calculated using the following equation:

\[
\text{STH} (\%) = \frac{J_{op} \times 1.23 \times \eta_F}{P_{in}}
\]

, where \(J_{op}\) is the operating photocurrent density (mA cm\(^{-2}\)), \(\eta_F\) is the Faradaic efficiency, and \(P_{in}\) is an incident solar power (100 mW cm\(^{-2}\)).

### Computational details

The spin-polarized DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave method for the core region and a plane-wave kinetic energy cutoff of 400 eV. The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation potentials was used. The DFT + U calculations were performed with Hubbard–U correction of \(U = 3.25\) eV to the \(d\)-electrons of Bi to account for the on-site correlation effects. A \(7 \times 5 \times 7\) gamma-centered Monkhorst-pack sampled \(k\)-point grid was employed to sample the reciprocal space for the bulk BiVO\(_4\). Monkhorst-pack \(k\)-point meshes of \(2 \times 2 \times 1\) were used for structure optimization and property calculation BiVO\(_4\) (010) slab, CPF-TCB, and the heterojunction CPF-TCB/BiVO\(_4\) (010) heterostructure. The large vacuum layers of these slab models were set at least 15 Å in the \(z\)-direction for the isolation of the surface to prevent the interaction between two periodic units. The optimized lattice constants of BiVO\(_4\) were \(a = 7.338\) Å, \(b = 11.727\) Å, \(c = 5.188\) Å, \(\alpha = \gamma = 90.00^\circ\), and \(\beta = 135.01^\circ\), respectively. The surface of BiVO\(_4\) (010) was carried out using the slab model composed of \(4 \times 3\) supercells with four metal atomic monolayers. The bottom two atomic monolayers of BiVO\(_4\) (010) were fixed at their bulk positions while the rest atomic layers and 2-dimensional CPF-TCB layer were free to move in all directions until the convergence of energy and residual force on each atom were less than \(1 \times 10^{-6}\) eV Å\(^{-1}\) and \(0.05\) eV Å\(^{-1}\), respectively. To describe the charge transfer process in the CPF-TCB/BiVO\(_4\) heterostructure, the dipole moment on the \(z\)-direction was calculated, and planar averaged charge density was acquired by averaging charge density on the \(xy\) plane toward the \(z\)-direction.

### Data availability

All data supporting the findings of this study are available within the main text and the ESL. All relevant data are available from the corresponding authors upon reasonable request.

### Author contributions

H. W. J., J. Y. K., J. M., and M. S. K. supervised the project. H. W. J. and J. W. Y. conceived the project and designed the experiments. J. W. Y. fabricated and measured the devices and analyzed the experimental results. S. G. J. fabricated perovskite/Si solar cells. C. S. J. fabricated perovskite photocathodes. J. K performed density functional theory calculations and helped to analyze X-ray absorption spectra. H. R. K. helped to analyze the carrier dynamics. T. H. L. carried out transmission electron microscopic characterizations. S. A. L. helped to analyze the experimental results. W. S. C. conducted gas chromatography measurements. S. L. helped to synthesize conjugated polymers. H. L. helped to measure the photocathode. J. W. Y. and H. W. J. mainly wrote the manuscript. All authors discussed the results and commented on the manuscript at all stages.

### Conflicts of interest

The authors declare no competing interests.

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