Efficient and Ultrastable Iodide Oxidation Reaction Over Defect-Passivated Perovskite Photoanode for Unassisted Solar Fuel Production

Juwon Yun, Young Sun Park, Hyungsoo Lee, Wooyong Jeong, Chang-Seop Jeong, Chan Uk Lee, Jeongyoub Lee, Subin Moon, Eunji Kwon, Soobin Lee, Sumin Kim, Junhwan Kim, Seungho Yu, and Jooho Moon*

Recently, lead halide perovskites have emerged as promising photoanode materials for efficient hydrogen production. However, the sluggish kinetics of the oxygen evolution reaction (OER) and interfacial defect-mediated charge accumulation inevitably result in efficiency loss and degradation of perovskite photoanodes. Herein, a defect-passivated electron transport layer-based perovskite photoanode combined with a catalyst layer favorable is introduced for iodide oxidation reaction bearing a small thermodynamic barrier and rapid kinetics compared to OER for efficient solar fuel generation. The resulting perovskite photoanode revealed a saturated photocurrent density of 22.4 mA cm$^{-2}$ at 0.3 V versus the reversible hydrogen electrode (V_RHE) with an impressive onset potential of $-0.2$ V_RHE as well as durability for 225 h in a neutral electrolyte. In addition, an unbiased hydrogen-production device comprising a perovskite photoanode and Pt coil electrocatalyst is demonstrated, achieving a remarkable solar-to-chemical conversion efficiency of 11.45% and stable operation for 25 h. Moreover, a wireless artificial leaf-structured device realizing solar-driven hydrogen generation in natural sea water under outdoor sunlight is presented.

1. Introduction

With an aim to reach carbon zero by 2050 as declared in the Paris Agreement, it is currently the most vital issue to mitigate global warming. Accordingly, eco-friendly, sustainable energy sources need to be urgently developed to replace carbon-based energy sources. Unassisted photoelectrochemical (PEC) hydrogen production is a promising candidate to achieve carbon zero.[1–3] However, compared to efficient photocathode materials such as Sb$_2$Se$_3$, Cu$_2$O, and SnS, recently reported photoanodes have suffered from unsatisfactory efficiency owing to inferior light absorption and low charge-separation capability, posing an obstacle for practical unbiased hydrogen generation.[3–8] These limitations are fundamentally attributed to the large bandgap, short minority carrier diffusion length, and low carrier mobility of the semiconductors used in conventional photoanodes (e.g., BiVO$_4$, Fe$_2$O$_3$, Ta$_3$N$_5$, Sb$_2$S$_3$, and WO$_3$).[9] Although various approaches, including nanostructuring, doping, and interface engineering, have been adopted to overcome the limitations, the efficiency of state-of-art photoanodes still remains insufficient.[10–14] Thus, it is indispensable to explore promising photoanode materials that enable efficient oxidation half-reaction for hydrogen generation.

Recently, lead halide perovskites have emerged as a new breakthrough to overcome the limitations of conventional photoanode materials owing to their tunable bandgaps, excellent hole mobility, and long hole-diffusion length.[15] While it is vulnerable to moisture, various studies have reported the development of various protective layers and conductive materials to minimize the performance loss.[16] These advancements have enabled the perovskite photoanode to achieve the superior performance and enhanced operational stability in aqueous environments.[17,18] In addition, recent researches demonstrated the importance of a defect-passivated electron transport layer (ETL) in a perovskite photoanode for suppressing undesirable efficiency loss.
and degradation of the perovskite absorber induced by a charge accumulation at the ETL.\textsuperscript{[19,20]} The resulting perovskite photoanode for OER yielded an improved onset potential of 0.34 V with respect to reversible hydrogen electrode (V\textsubscript{RHE}) and remarkable durability for 225 h, maintaining \textasciitilde70% of the initial photocurrent density in an alkaline electrolyte. However, an unsatisfactory onset potential still remains an obstacle for competitive solar-driven photosynthesis. The relatively high onset potential originates from the fact that OER requires a high thermodynamic potential (1.23 V\textsubscript{RHE}) and involves four-electron transfer steps, leading to its sluggish kinetics.\textsuperscript{[21]} Moreover, interfacial charges accumulation owing to slow kinetics causes the degradation of the perovskite.\textsuperscript{[19]} In this regard, it is highly desirable to replace the OER with an alternative oxidation reaction characterized by a lower oxidation potential and faster kinetics.

Among the various anodic reactions as alternatives to OER, the iodide oxidation reaction (IOR) has emerged as an attractive oxidation half-reaction.\textsuperscript{[16,22,23]} IOR requires a small thermodynamic oxidation potential of 0.54 V with respect to normal hydrogen electrode (V\textsubscript{NHE}), which corresponds to a 0.954 V\textsubscript{RHE} in a neutral electrolyte (i.e., naturally available seawater or rainwater) as expressed by the following equation:\textsuperscript{[24]}

\[ V_{RHE} = V_{NHE} + 0.05916 \times \text{pH} \]  

Indeed, recent works have demonstrated that the oxidation potential required for anodic reaction could be effectively mitigated by employing IOR instead of OER.\textsuperscript{[25–27]} Moreover, IOR exhibits rapid reaction kinetics due to its facile two-electron transfer step in neutral media, generating valuable products (i.e., iodine) that are widely used in the hygiene industry and zinc–iodine batteries.\textsuperscript{[28,29]} This fast kinetics of IOR even in a neutral medium, where OER exhibits much slower kinetics than in an alkaline medium owing to the low hydroxide concentration, would enable an efficient and durable perovskite photoanode suitable for real-world applications. Despite these thermodynamic and kinetic advantages, there are no studies on the perovskite-based photoanode to achieve PEC iodide oxidation. Thus, a defect-passivated ETL-based perovskite photoanode combined with an IOR-oriented optimized catalyst could present a breakthrough for efficient solar fuel production.

Herein, we report a solar fuel device based on a combination of a perovskite-based photoanode and Co-doped Ni\textsubscript{3}S\textsubscript{2} IOR electrocatalyst. To fabricate an efficient and durable perovskite photoanode, the inherent defects are passivated by 4-methoxyphenethylamine (MPA) comprising a benzene-ring structure with amine and methoxy functional groups, which effectively coordinate with the surface defects of the ETL and perovskite, respectively. The MPA treatment also adjusts the band alignment between the ETL and perovskite, alleviating charge accumulation at the perovskite/ETL interface. Subsequently, hydrothermally synthesized Co-doped Ni\textsubscript{3}S\textsubscript{2} catalyst having intrinsic iodide oxidation capability is applied on top of a Ni foil encapsulation layer. This rationally designed perovskite photoanode exhibits a saturated IOR photocurrent density of 22.4 mA cm\textsuperscript{-2} at 0.3 V\textsubscript{RHE} with an onset potential of \textasciitilde0.2 V\textsubscript{RHE} in a neutral electrolyte. Furthermore, the lifetime of our perovskite photoanode is substantially extended (225 h), maintaining \textasciitilde90% of the initial photocurrent density. We also accomplish an efficient unbiased hydrogen-production system in a configuration of IOR-driving perovskite photoanode combined with a Pt coil electrocatalyst (EC) for hydrogen evolution reaction (HER), exhibiting a high solar-to-chemical conversion (SCC) efficiency of 11.45% and stable operation for 25 h. Moreover, a wireless artificial leaf for the unassisted photosynthesis of hydrogen in natural sea water is successfully demonstrated for the first time using our perovskite photoanode under outdoor sunlight, suggesting a novel pathway for practical exploitation.

2. Results and Discussion

Figure 1a depicts a schematic device configuration of the perovskite photoanode fabricated in this study. The device structure of the photoanode is identical to that of a solar cell except for the catalyst/encapsulation layer. The n-i-p-type perovskite solar cell (PSC) was composed of Au/spiro-OMeTAD/perovskite/SnO\textsubscript{2}/fluorine-doped tin oxide (FTO). A lead halide perovskite with a composition of (FAPb\textsubscript{1}I\textsubscript{3.95}MAPbBr\textsubscript{0.05} (denoted as PSK) was employed as an absorber layer. SnO\textsubscript{2} and spiro-OMeTAD were employed as the ETL and hole transport layer, respectively. Ni foil was employed as an encapsulation layer on top of Au electrode to prevent water permeation, and carbon powder was also inserted to ensure electrical contact between the Ni foil and Au electrode. Subsequently, the Co-doped Ni\textsubscript{3}S\textsubscript{2} catalyst was attached to the Ni foil of the PSK photoanode. To suppress undesired efficiency loss of the PSK photoanode, MPA was decorated onto SnO\textsubscript{2} ETL (denoted as MPA-SnO\textsubscript{2}) by spin-coating; the details are given in the Experimental section. When the device was fabricated without interface treatment, it was referred to as a bare SnO\textsubscript{2} device. To evaluate the MPA treatment effect, we measured the performance of the photoanode in the form of a solar cell because the photocarrier generation and extraction to the electrode were identical in both PSC and PSK photoanodes, except for an additional electrochemical reaction at the electrolyte/electrode (catalyst) interface in the photoanode. The champion performances of bare SnO\textsubscript{2} and MPA-SnO\textsubscript{2}-based PSCs are shown in Figure 1b. The bare SnO\textsubscript{2} device showed a maximum power conversion efficiency (PCE) of 19.77% with an open-circuit voltage (V\textsubscript{OC}) of 1.11 V, a short-circuit current density (J\textsubscript{SC}) of 22.40 mA cm\textsuperscript{-2}, and a fill factor (FF) of 79.85%. By contrast, the PSC with MPA-SnO\textsubscript{2} exhibited higher performance than the bare SnO\textsubscript{2} device, revealing a maximum PCE of 22.61% with a V\textsubscript{OC} of 1.14 V, J\textsubscript{SC} of 23.83 mA cm\textsuperscript{-2}, and FF of 83.00%. The corresponding external quantum efficiency (EQE) was greater than 85% in the wavelength range of 350–800 nm and the integrated J\textsubscript{SC} was 23 mA cm\textsuperscript{-2}, which showed a slight deviation from the value obtained from the J–V curve (Figure S1, Supporting Information). We evaluated the performance by varying the MPA concentration (5, 10, and 20 mg mL\textsuperscript{-1}) to optimize the interface treatment (Figure S2, Supporting Information). In addition, the performance statistics for PSCs were obtained from 15 separately fabricated devices as a function of MPA treatment concentration, revealing reproducible performance (Figure S3, Supporting Information). The average PCE increased in the order of bare SnO\textsubscript{2} <
Figure 1. a) Device structure of the PSK photoanode in a configuration of Co-Ni$_3$S$_2$/Ni foam/Ni foil/carbon powder/Au/spiro-OMeTAD/PSK/MPA-SnO$_2$/FTO. b) $J$–$V$ curves of the champion PSCs based on bare SnO$_2$ and MPA-SnO$_2$. c) PCE distribution diagram of PSCs under variation of the MPA concentration. d) Normalized PCE versus storage time for the encapsulated PSCs based on bare SnO$_2$ and MPA-SnO$_2$.

$\text{MPA(5 mg)}$-SnO$_2$ < $\text{MPA(20 mg)}$-SnO$_2$ < $\text{MPA(10 mg)}$-SnO$_2$ (Figure 1c). Figure 1c reveals that at the MPA concentration of 5 mg mL$^{-1}$, the MPA surface coverage on SnO$_2$ may be incomplete, while the thicker MPA layer acts as a series resistance at 20 mg mL$^{-1}$, inhibiting the electron extraction at PSK/SnO$_2$ interface. In this regard, the MPA treatment at the concentration of 10 mg mL$^{-1}$ allows an optimal thickness of the MPA-SnO$_2$-based PSC. In particular, the average $J_{\text{SC}}$ and FF values significantly improved at the optimal MPA concentration. These enhanced $J_{\text{SC}}$ and FF values play a critical role in determining the operation point of an unbiased PEC photoelectrode device. Hysteresis behavior was also evaluated to understand the amount of charge accumulation at the PSK/ETL interface (Figure S4, Supporting Information).$^{[30]}$ The $J$–$V$ curves were measured at various scan rates, including low rate (0.08 V s$^{-1}$), intermediate rate (0.5 V s$^{-1}$), and fast rate (2.5 V s$^{-1}$). The hysteresis index (HI) is calculated as follows:

$$HI = \frac{\text{PCE}_{\text{reverse}} - \text{PCE}_{\text{forward}}}{\text{PCE}_{\text{reverse}}}$$

(2)

where $\text{PCE}_{\text{forward}}$ and $\text{PCE}_{\text{reverse}}$ represent PCE values obtained from forward and reverse scans, respectively. As shown in Figure S4 (Supporting Information), hysteresis was commonly observed for all scan rates, regardless of the MPA treatment. However, the magnitude of hysteresis and HI were significantly lowered depending upon the MPA treatment. According to a previous report, hysteresis can be suppressed by reducing the recombination rates and defect densities.$^{[31]}$ Therefore, it is speculated that the MPA treatment effectively mitigates the mobile ions by...
defect passivation. The performance of both MPA-treated and bare SnO2 PSC devices was measured using the maximum power point tracking method to evaluate their long-term stability under ambient atmosphere (relative humidity below 30%). After 50 days, the MPA-SnO2 device maintained ≈85% of its initial PCE, while the bare SnO2 device showed significant degradation, with the PCE decreasing to ≈70% of its initial value (Figure 1d). Therefore, it can be inferred that the superior stability of the MPA-SnO2 PSC compared to its bare SnO2 counterpart is attributable to the improved quality of the PSK/SnO2 interface by MPA treatment, resulting in the alleviated charge accumulation as well as less ion migration.[32] Therefore, MPA treatment will likely facilitate electron extraction, resulting in the enhanced performance and better stability of the PSK photoanode.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the surface chemical states of SnO2 after MPA treatment (i.e., bare SnO2 and MPA-SnO2). The Sn 3d3/2 and 3d5/2 peaks were located at 495.4 and 486.9 eV for the bare SnO2 film (Figure 2a).[33] When MPA was decorated on SnO2, Sn 3d3/2 and 3d5/2 peaks shifted to 486.7 and 495.2 eV, respectively, showing a negative shift of 0.2 eV with respect to the bare SnO2 film, indicating that the electron density of Sn increases after MPA treatment.[34] The presence of oxygen vacancies and hydroxyl groups on SnO2 represents surface defects, which hinder the charge transport and deprotonate the perovskite structure.[35,36] For a clear observation of the variation in chemical states after MPA treatment, the O 1s XPS spectra are shown in Figure 2b,c. The O 1s peaks are deconvoluted at ≈530.8 and ≈532 eV. The peak at 530.8 eV is attributed to Sn-O, and the other peak at 532 eV is ascribed to the surface defects of SnO2 (i.e., oxygen vacancies and hydroxyl groups).[37] The peak area fraction of surface defects over the total O 1s peak area (lattice oxygen + oxygen vacancy) was 0.52 for bare SnO2 (Table S1, Supporting Information). By contrast, the peak area fraction of surface defects significantly decreased to 0.37 for the MPA-SnO2 film. The methoxy group in MPA is capable of donating electrons to SnO2 while acting as a Lewis base to coordinate with Lewis acids such as unsaturated Sn metal and oxygen vacancies.[38] Therefore, MPA treatment effectively passivates the surface defects of SnO2. Moreover, it has been reported that the protonated amine group (NH3+2) in MPA-treated SnO2 is capable of passivating PbI2 antiseptic defects and reducing trap states of perovskite owing to electrostatic interactions (Figure S5, Supporting Information).[39] The reduced defects of SnO2 and PSK likely facilitate the carrier extraction while lowering the possibility for charge accumulation at the PSK/SnO2 interface. X-ray diffraction (XRD) was performed to determine PSK crystallinity (i.e., PSK/bare SnO2/FTO and PSK/MPA-SnO2/FTO) after MPA treatment. Nearly identical XRD peaks were observed regardless of MPA treatment, suggesting that interface treatment neither alters the PSK crystallinity nor induces the formation of a 2D phase or intermediate phase (Figure S6, Supporting Information).[40] Scanning electron microscopy (SEM) revealed that all PSK samples exhibited nearly similar morphology (Figure S7, Supporting Information). Therefore, it can be concluded that MPA treatment only affects the electronic properties of SnO2. Topography and current mapping images obtained by conductive atomic force microscopy (c-AFM) are shown in Figure S8 (Supporting Information). Both bare SnO2

Figure 2. XPS spectra of SnO2/FTO under MPA treatment (i.e., bare SnO2 and MPA-SnO2): a) Sn 3d and b) and c) deconvolution of O 1s regions. Scatter points represent the experimental results, while solid lines denote the fitted data. d) Capacitance (Csc) variation versus applied voltage presented in the Mott–Schottky plot for PSCs based on bare SnO2 and MPA-SnO2 in the dark. e) Steady-state PL and f) TRPL spectra of PSK deposited on SnO2/FTO as a function of MPA treatment.
and MPA-SnO2 films revealed almost identical surface topographies and roughness. The presence of the MPA layer caused negligible changes in the morphology of SnO2 as confirmed by SEM results. The root-mean-square roughness ($R_q$) were almost identical, indicating that MPA treatment conformally decorated the surface of SnO2. However, in current mapping images at $\approx 5$ V, MPA-SnO2 showed a much higher current than bare SnO2, because MPA treatment raised the conductivity of SnO2 owing to its conjugated MPA molecule, thus making it capable of facilitating charge transport at the PSK/SnO2 interface.\(^{[19]}\)

The band position of bare-SnO2 and MPA-SnO2 was investigated by ultraviolet photoelectron spectroscopy (UPS) measurements (Figure S9, Supporting Information). The Fermi level of bare SnO2 was calculated by UPS as $\approx -4.68$ eV versus vacuum (following the equation (1)), whereas Fermi level of MPA-SnO2 ($\approx -4.47$ eV vs vacuum) is lower than that of bare SnO2. This result indicates that the MPA layer induces an upward shift of the SnO2 band energy and lowers the conduction band of bare SnO2 film. The energy level diagram was obtained in Figure S10 (Supporting Information) based on the UPS results and previous report.\(^{[37]}\) The magnitude of the built-in potential ($V_{\text{bi}}$) of the bare SnO2 and MPA-SnO2 devices (i.e., Au/spiro-OMeTAD/perovskite/(MPA)-SnO2/FTO solar cell configuration) was determined by Mott–Schottky analysis. The Mott–Schottky analysis was performed under a fixed frequency (10 kHz) and dark condition (Figure 2d). The calculated capacitance was a reasonable value compared to those in previous reports.\(^{[41]}\) The $V_{\text{bi}}$ of the MPA-SnO2 device increased from 0.92 to 1.02 V compared to the bare SnO2 device. This observation indicates that MPA treatment intensifies the band bending of the MPA-SnO2 device, resulting in an increase in $V_{\text{bi}}$ which well correlates with the UPS result (Figure S9, Supporting Information).\(^{[41]}\) Compared to our previous work, the MPA molecule provides simplified interface engineering.

The influence of interface engineering on the carrier dynamic was characterized by the steady-state photoluminescence (PL) in PSK/bare SnO2/FTO and PSK/MPA-SnO2/FTO (Figure 2e). The emission peak around 780 nm commonly appeared in all PSK samples. The absorption spectra of the PSK film, shown in Figure S11 (Supporting Information), revealed an absorption edge at $\approx 780$ nm, corresponding to the position of the PL emission peak. This result indicated that the PSK demonstrates highly efficient light absorption and emission processes, as evidenced by the previous work.\(^{[37]}\) This PL emission was remarkably reduced for the MPA-SnO2 sample compared to the bare SnO2 sample, implying that the charge carrier transport is enhanced in the MPA-SnO2 sample owing to the passivation of defects on SnO2.\(^{[42]}\) To further investigate the carrier extraction at the PSK/SnO2 interface, time-resolved photoluminescence (TRPL) measurements were conducted (Figure 2f). A double-exponential decay function was used to fit the TRPL spectra; the obtained fitting results are listed in Table S2 (Supporting Information). The carrier lifetime of the MPA-SnO2 sample ($\tau_{\text{ave}} = 142.8$ ns) was shorter than that of the bare SnO2 sample ($\tau_{\text{ave}} = 483.2$ ns). This observation suggests the improvement in electron extraction at the PSK/SnO2 interface through MPA treatment.\(^{[37]}\) Furthermore, transient photocurrent spectra (TPC) showed faster photocurrent decay in the MPA-SnO2 device than in the bare SnO2 device (i.e., Au/spiro-OMeTAD/perovskite/(MPA)-SnO2/FTO), which is well matched with the PL and TRPL results (Figure S12, Supporting Information).\(^{[20]}\) Thus, MPA treatment on SnO2 effectively passivates the defects on SnO2 and improves the charge carrier transport capability, which will eventually result in an efficient and stable PSK-based photoanode.

Although the optoelectrical properties of PSK are noticeably improved by interface engineering, a catalyst compatible with IOR is indispensable for the PSK photoanode to drive efficient PEC iodide oxidation. A Ni$_3$S$_2$-based catalyst was deposited on commercial Ni foam via a hydrothermal process (please see the Experimental Section for details). Furthermore, Co was incorporated into Ni$_3$S$_2$ by dissolving CoCl$_2$·6H$_2$O in a precursor solution during the hydrothermal synthesis. Co doping has been reported to induce lattice distortion, enhancing active sites as well as modifying the electronic structure, which triggers the regulation of adsorption/desorption energies of intermediates.\(^{[34,44]}\) The 0.2 mmol of Co atoms were added in the precursor solution, and the resulting catalyst on Ni foam was denoted as the Co-Ni$_3$S$_2$ electrode. Subsequently, the microstructures of undoped Ni$_3$S$_2$ and Co-Ni$_3$S$_2$ electrodes were investigated by SEM analysis, indicating that nanosheets arrays were evenly distributed on the Ni foam (Figure 3a). Interestingly, the undoped Ni$_3$S$_2$ exhibited large nanosheets, whereas the Co-Ni$_3$S$_2$ electrode revealed small nanosheets with porous structures. This difference was possibly caused by the structural distortion induced by the incorporation of Co, inhibiting the crystallization of Ni$_3$S$_2$ nanosheets.\(^{[45]}\) To scrutinize the crystallographic information of two different electrodes, XRD measurement was conducted as shown in Figure 3b. Most of the diffraction peaks were consistent with standard hexagonal Ni$_3$S$_2$. The crystallinity of Ni$_3$S$_2$-based electrodes decreased as Co was added, which is well matched with the small nanosheets of Co-incorporated Ni$_3$S$_2$ electrodes (Figure 3a). This low crystallinity caused by structural distortion could create abundant active sites for electrochemical reactions.

XPS analysis was conducted to elucidate the surface electronic structure of Ni$_3$S$_2$-based electrodes. As shown in Figure 3c, the XPS spectra of Ni 2p exhibits two peaks at 853.1 and 870.4 eV corresponding to Ni$^{2+}$ derived from Ni–Ni metallic bonds in Ni$_3$S$_2$.\(^{[46,47]}\) Because of the incorporation of Co, the intensities of Ni$^{2+}$ peaks were reduced. This is because Co atom substitutes the Ni site, leading to a decrease in Ni–Ni metallic bonds.\(^{[47]}\) Additionally, the Ni$^{2+}$ 2p$_{3/2}$ and Ni$^{2+}$ 2p$_{1/2}$ peaks in Ni$_3$S$_2$, originally located at 873.3 and 855.5 eV, respectively, exhibited a distinct downward shift (0.2 eV) upon the incorporation of Co.\(^{[48]}\) The reason for this downward shift is that electrons are transferred from Co to Ni because of the higher electronegativity of Ni compared to that of Co.\(^{[49–51]}\) In the Co 2p spectra for Co-Ni$_3$S$_2$, the peaks located at 796.4 and 780.5 eV coincide with the peaks of Co$^{2+}$ 2p$_{3/2}$ and Co$^{2+}$ 2p$_{1/2}$, evidencing the existence of Co atoms (Figure S13a, Supporting Information).\(^{[52]}\) Furthermore, the S 2p spectra displayed two peaks near 162.0 and 163.1 eV assign able to the S$^2-$ species in the lattice of Ni$_3$S$_2$ (Figure S13b, Supporting Information).\(^{[53]}\) XPS analysis confirmed that the Co atoms successfully doped the Ni$_3$S$_2$ lattice. To further elucidate the crystallographic structure and elemental composition of Co-Ni$_3$S$_2$, transmission electron microscopy (TEM) was conducted. Figure 3d illustrates the low-magnification TEM image of
Co-Ni$_3$S$_2$, exhibiting the nanosheet structure. As shown in Figure 3e, the high-resolution TEM (HR-TEM) image of Co-Ni$_3$S$_2$ revealed a lattice fringe with an interplanar spacing of 0.27 nm attributable to the lattice distance of the (110) plane of Ni$_3$S$_2$, which is in good agreement with the XRD result. In addition, the scanning transmission electron microscopy (STEM) image and energy-dispersive X-ray spectroscopy (EDX) mapping verified the uniform distribution of elemental Ni, Co, and S on the Co-Ni$_3$S$_2$ nanosheets (Figure 3f).

The electrocatalytic activities of the Ni$_3$S$_2$-based electrodes for IOR were evaluated in 0.5 M KPi buffer electrolyte containing 0.5 M KI (pH 6.5) by employing a three-electrode system. As seen in the linear sweep voltammetry (LSV) curves, the potentials required to achieve a current density of 10 mA cm$^{-2}$ for iodide...
oxidation were 1.02 and 0.97 V_{RHE} for undoped Ni_{3}S_{2} and Co-Ni_{3}S_{2}, respectively (Figure 4a). We further measured the IOR catalytic capability of Ni_{3}S_{2}-based electrodes prepared by varying the Co doping concentration (e.g., 0.1, 0.2, 0.3, and 0.4 mmol), confirming that the optimal concentration of Co was 0.2 mmol (Figure S14, Supporting Information). Notably, Ni_{3}S_{2}-based electrodes displayed sole IOR catalytic activity because the bare Ni foam revealed inferior iodide oxidation capability (Figure S15, Supporting Information). The Tafel slopes of undoped Ni_{3}S_{2} and Co-Ni_{3}S_{2} for IOR were estimated to be 64.6 and 54.9 mV dec^{-1}, demonstrating rapid electrochemical reaction kinetics of Co-Ni_{3}S_{2} compared to the undoped Ni_{3}S_{2} electrode (Figure 4b).

The LSV curve of Co-Ni_{3}S_{2} for OER was also obtained in KPi buffer electrolyte without the presence of KI to elucidate the different catalytic capabilities of Co-Ni_{3}S_{2} for OER with respect to IOR (Figure S16, Supporting Information). The slightly increased current density under a potential less than 1.6 V_{RHE} was attributed to the oxidation of Ni^{2+} to Ni^{3+}, and the current density was rapidly enhanced beyond 1.6 V_{RHE} owing to the occurrence of OER.[9] Impressively, the oxidation potential required to deliver a current density of 10 mA cm^{-2} for IOR was 0.7 V lower than that for OER, implying that IOR is more energetically favorable than OER in a neutral electrolyte. Electrochemical impedance spectroscopy (EIS) was performed at 0.95 V_{RHE} to investigate the charge transfer property of IOR driven by Ni_{3}S_{2}-based electrodes (Figure 4c). A Randles–Ershler circuit model comprising a series resistance (R_s), charge transfer resistance (R_{ct}), and constant-phase element was used for fitting the results of EIS measurement (inset of Figure 4c). The Nyquist plots of the two different electrodes displayed a single semicircle at low frequencies, corresponding to the R_{ct} representing the catalytic capability for IOR. The fitted results demonstrated that Co-Ni_{3}S_{2} showed lower R_{ct} than the undoped Ni_{3}S_{2} electrode (Table S3, Supporting Information), indicating that Co-Ni_{3}S_{2} possesses superior IOR catalytic ability compared to the undoped Ni_{3}S_{2} electrode, which is consistent with the LSV results.
The cyclic voltammetry (CV) curves of Ni$_3$S$_2$-based electrodes were obtained at various scan rates to determine the electrochemical active surface area (ECSA), which is an indispensable factor closely related to electrocatalytic activities (Figure S17a,b, Supporting Information). The double-layer capacitance ($C_{dl}$) estimation based on ECSA suggested that the Co-Ni$_3$S$_2$ exhibited a higher $C_{dl}$ of 2.0 mF cm$^{-2}$ with respect to undoped Ni$_3$S$_2$ (1.5 mF cm$^{-2}$), indicative of enlarged catalytic surface area upon the existence of Co atoms in the Ni$_3$S$_2$ lattice (Figure S17c, Supporting Information). This observation supports the fact that the incorporated Co atoms result in porous structures as well as lattice distortion of Ni$_3$S$_2$, leading to enhanced active site densities. In addition, the specific activity ($J_s$) corresponding to specific current density per ECSA was obtained to compare the intrinsic IOR activities as expressed by the following equations:

$$J_s = \frac{J_f \times A}{ECSA}$$  
(3)

$$ECSA = \frac{C_{dl}}{C_s}$$  
(4)

where $A$ is the geometric area of the Ni$_3$S$_2$-based electrodes, $J_f$ is the current density per geometric area of the electrode, and $C_s$ is the specific capacitance with identical values for both the electrodes, because they drive IOR under the same electrolyte.\[22,56\]

The obtained $J_s$ of Co-Ni$_3$S$_2$ showed a larger value compared to that of undoped Ni$_3$S$_2$, suggesting that Co doping promotes the density of active sites as well as inherent IOR catalytic activity of Ni$_3$S$_2$ (Figure S18, Supporting Information). Further, the long-term stability of the Co-Ni$_3$S$_2$ electrode for IOR was evaluated (Figure 4d). To mitigate the effect of iodide concentration variation during the stability test, chronoamperometry was conducted using a three-electrode system without a membrane to separate the working and counter electrodes. Hence, iodine molecules generated at the working electrode underwent partial reduction to form iodide at the counter electrode, thereby maintaining nearly constant iodide concentration.\[22,28\] During the chronoamperometric test, the Co-Ni$_3$S$_2$ electrode maintained an initial current density of 20 mA cm$^{-2}$ without obvious deterioration for 150 h, demonstrating the remarkable durability for IOR in a neutral electrolyte. The wave-like fluctuation of the current density for Co-Ni$_3$S$_2$ was attributed to fluxion as well as evaporation of electrolyte, since the electrolyte was magnetically stirred at 400 rpm to enhance mass transfer.

Density functional theory (DFT) analysis was performed to investigate the superior intrinsic iodide oxidation activity of Co-Ni$_3$S$_2$ with respect to undoped Ni$_3$S$_2$. On the basis of XRD and TEM results, the metal sites of the (110) surface of Ni$_3$S$_2$-based electrodes were selected as the active site for enabling IOR. The adsorption/desorption behaviors of the reactant on the metal sites of undoped Ni$_3$S$_2$ and Co-Ni$_3$S$_2$ were determined to evaluate the intrinsic IOR catalytic capability (Figure S19, Supporting Information). As shown in Figure 4e, the Gibbs free-energy diagram of IOR for Ni$_3$S$_2$-based catalysts illustrates a high overpotential of 0.68 eV for the adsorption of iodides on the Ni site contained in undoped Ni$_3$S$_2$. By contrast, the iodide anions are favorably adsorbed on the Co site of Co-Ni$_3$S$_2$ with a low overpotential of 0.58 eV. This is attributed to high valence state of Co induced by the electron transfer from Co to Ni as confirmed by XPS results. The low energy barrier derived from Co sites enables the improved intrinsic IOR activity of Co-Ni$_3$S$_2$ relative to undoped Ni$_3$S$_2$. Moreover, additional calculations were performed to investigate the adsorption energy at the Ni sites neighboring the Co site in Co-Ni$_3$S$_2$ (Figure S20, Supporting Information). The overpotential for IOR at the Ni sites of Co-Ni$_3$S$_2$ was $\approx$0.68 eV. While iodide anions were favorably adsorbed on the Co site of Co-Ni$_3$S$_2$ with lower overpotential, similar overpotential values were observed between the Ni site of Ni$_3$S$_2$ and Ni site of Co-Ni$_3$S$_2$. According to EDX analysis, it was confirmed that the molar ratio of Co/(Co+Ni) in Co-Ni$_3$S$_2$ was calculated to 23.6% which is undeniable value (Table S4, Supporting Information). Therefore, Co-Ni$_3$S$_2$ could reduce the overpotential for IOR due to the substantial quantity of Co site, despite of negligible difference in the energy barriers for IOR at the Ni sites between Co-Ni$_3$S$_2$ and Ni$_3$S$_2$.

After optimizing the PSK-based solar cell and IOR catalyst, we fabricated a PSK-based photoanode. The champion IOR performance of PSK photoanode integrated with Co-Ni$_3$S$_2$ catalyst was characterized by LSV under 1-sun illumination in 0.5 m KPi buffer electrolyte containing 0.5 m KI (Figure 5a). Considering the work functions of Ni metal (5.0 eV) and Ni$_3$S$_2$-based catalyst (4.96 eV) reported by previous research as well as band energy illustration of PSC in Figure S10 (Supporting Information) the energy-level diagram of Co-Ni$_3$S$_2$/PSK photoanode is shown in Figure S21a (Supporting Information). Therefore, the photogenerated holes and electrons of Co-Ni$_3$S$_2$/PSK are separated along the band bending and reach the Co-Ni$_3$S$_2$ electrode and the bottom FTO electrode, respectively. Subsequently, the holes migrate to the electrolyte, thereby contributing to the IOR, while the electrons transfer to the counter electrode (i.e., Pt coil) via the external circuit, enabling HER (Figure S21b, Supporting Information). The performance of the Co-Ni$_3$S$_2$/PSK device was significantly improved compared to the PSK photoanode without a catalyst. The Co-Ni$_3$S$_2$/PSK photoanode showed a remarkable onset potential of $-0.2$ V$_{RHE}$ along with a saturation photocurrent density of 22.4 mA cm$^{-2}$ at 0.2 V$_{RHE}$. The PSK photoanode without Co-Ni$_3$S$_2$ catalyst was encapsulated with Ni foil, therefore the Ni foil was contacted with electrolyte during the IOR. Accordingly, the Ni metal could serve as catalyst for driving IOR. As shown in Figure S15 (Supporting Information), the Ni foam displayed IOR onset potential of 1.4 V$_{RHE}$ which is 0.47 V higher than that of Ni$_3$S$_2$ electrode. This value is nearly identical with the onset potential difference between Co-Ni$_3$S$_2$/PSK and PSK photoanodes (Figure 5a). Moreover, the Tafel slope of Ni foam exhibited 180.0 mV dec$^{-1}$ which is significantly larger value than that of Co-Ni$_3$S$_2$ (54.9 mV dec$^{-1}$), implying sluggish IOR kinetics of Ni metal (Figure S22, Supporting Information). Therefore, the enhancement of photocurrent density at low potential was originated from the rapid IOR kinetics of Co-Ni$_3$S$_2$ catalyst. In addition, the photoanode with MPA-SnO$_2$ showed higher performance than the bare SnO$_2$ photoanode, which well matches with PSC performance (Figure S23, Supporting Information). We measured the open-circuit photovoltage (OCV) of the Co-Ni$_3$S$_2$/PSK photoanode to determine the photovoltage (Figure S24, Supporting Information). There was no significant OCV difference depending on the catalyst in which $\approx$ 1.05 V photovoltage commonly developed. In buried-junction photovoltaic, the
photovoltage is generated within the PSK junction with ETL and HTL, and its magnitude is independent of the catalyst placed outside the junction. The OCV values of PSK and Co-Ni$_3$S$_2$/PSK photoanode well correlates with the mean $V_{OC}$ value of the MPA-SnO$_2$ PSC. This observation indicates nearly no loss in both photovoltage and current despite a multilayered device structure. Compared to PSC, performance loss in the onset potential region was observed owing to an electrochemical reaction (IOR) at the electrolyte/electrode (catalyst) interface. Notably, the performance loss in IOR significantly decreased compared to that observed in OER (Figure S25, Supporting Information). This result could be attributed to the faster kinetics of IOR, which enables more efficient IOR-driven, rather than OER-driven, hydrogen production. The incident photon-to-current conversion efficiency (IPCE) of the Co-Ni$_3$S$_2$/PSK photoanode measured at 0.6 $V_{RHE}$ was over 80% in a wide wavelength range of 450–780 nm (Figure 5b). Moreover, the integrated photocurrent density from the IPCE was $\approx 19.3$ mA cm$^{-2}$. The slightly less integrated photocurrent density obtained from the IPCE measurement compared to the champion LSV result in Figure 5a is attributable to the absence of a stirring system.

To evaluate the PEC stability of the Co-Ni$_3$S$_2$/PSK photoanode, we conducted chronoamperometry measurement at 0.6 $V_{RHE}$ under continuous illumination without a membrane. The photocurrent density fluctuation induced by electrolyte fluxion and/or evaporation was intensified compared to chronoamperometric test of the Co-Ni$_3$S$_2$ catalyst (Figure 4d) because the temperature of electrolyte raised due to 1-sun illumination. Therefore, the electrolyte could be rapidly fluxed and evaporated compared to dark system, leading to the significant fluctuation of current density. Figure 5c reveals that the Co-Ni$_3$S$_2$/PSK device operated stably, retaining $\approx 90\%$ of its initial current density for 225 h. The sharp peaks were discovered at 27, 70, and 193 h during the chronoamperometric test. At those durations, we turned off the illumination and immediately turned back on to elucidate the existence of leakage current induced by side reaction. When the light turned off, the photocurrent density of Co-Ni$_3$S$_2$/PSK photoanode disappeared and recovered its initial value when the light turned back on. This result represents that our perovskite-based photoanode demonstrated the absence of any leakage current. The chemical states of the surface of Co-Ni$_3$S$_2$ were characterized by XPS analysis after electrolysis, indicating that there was no significant change in the chemical states (Figure S26, Supporting Information). By contrast, the PSK showed the degradation after stability test. In the XRD analysis of the PSK photoanode, a shift in the (100) plane's peak and the emergence of a PbI$_2$ phase were observed (Figure S27a, Supporting Information). Additionally, PL measurements revealed a red-shift in the PL peak toward a longer wavelength compared to the fresh sample (Figure S27b, Supporting Information). This shift is commonly associated with the migration of iodine ions, which often results in phase separation and material degradation, as supported by the previous study. Based on these results, it is speculated that degradation primarily originates from the perovskite material itself rather than the catalyst. The remarkable PEC efficiency as well as durability of the Co-Ni$_3$S$_2$/PSK photoanode for IOR even in an environmentally friendly neutral medium suggests the possibility of realistic solar fuel production. Furthermore, unlike in acidic electrolytes, which have been widely utilized in previous works on PEC IOR, the iodide ions are chemically stable in the neutral electrolyte, facilitating a more suitable operation condition for the photoanode. Interestingly, in the case of OER, the Co-Ni$_3$S$_2$/PSK
photoanode experienced a steep reduction to \( \approx 30\% \) of its initial current density within 2 h, exhibiting gradual degradation until 12 h at 0.6 V \( \text{RHE} \) (Figure S28, Supporting Information). This result indicates that the faster kinetics of electrochemical reaction at the electrolyte/catalyst interface improves the stability of the Co-Ni\(_3\)S\(_2\)/PSK photoanode.\(^{[19,20]}\) According to previous studies, hole accumulation induces the oxidation of iodine ions contained in the lattice of the PSK absorber, leading to the formation of PbI\(_2\) and degradation of the perovskite.\(^{[62]}\) Thus, the hole accumulation is remarkably reduced during IOR compared to OER. Additionally, the iodine and hydrogen products owing to IOR were quantified by employing an H-type cell with a Nafion 117 membrane separating the working/reference electrode in KPI electrolyte with dissolved KI (anolyte) from the counter electrode in pure KPI electrolyte (catholyte). This cell configuration was able to suppress iodine reduction at the counter electrode. The iodine production rate of the Co-Ni\(_3\)S\(_2\)/PSK photoanode calculated using the iodometric titration method was 10.11 \( \mu \text{mol h}^{-1} \) \(^{[63,64]}\) demonstrating \( \approx 90\% \) of faradaic efficiency, indicative of superior IOR capability (Figure S29, Supporting Information). Similarly, the average faradaic efficiency of hydrogen production driven by the counter electrode was evaluated by gas chromatography; it was calculated to be \( \approx 94\% \) (Figure S30, Supporting Information).

Subsequently, the PEC–EC tandem device, in which our PSK-based photoanode for IOR and Pt coil cathode for HER were connected as a two-electrode system without any reference electrode similar to the H-type cell, was fabricated to drive unassisted hydrogen production (Figure 6a). We successfully demonstrated unbiased solar-to-hydrogen conversion using the PEC–EC configuration comprising a combination of a single perovskite-based photoanode and EC, which affords a lower photovoltage than that of generally exploited multijunction perovskite-based photoanodes.\(^{[65,66]}\) As the IOR driven by the Co-Ni\(_3\)S\(_2\) catalyst effectively mitigates the overall required voltage for solar fuel production, our PEC–EC device could be operable without an external bias when paired with even a single perovskite photoanode. As shown in Figure 6b, the LSV curve of the PEC–EC system was obtained in the voltage range of \(-0.5\) to \(-0.5\) V under 1-sun illumination, delivering a noticeable operation photocurrent density of 12 mA cm\(^{-2}\) at 0 V under the bias-free condition. Our PEC–EC tandem device achieved a high hydrogen-production current density compared to recently reported unassisted solar-to-hydrogen conversion devices using low-cost material-based photoanodes (Table S5, Supporting Information). The SCC efficiency \((\eta_{\text{SC}})\) of our PEC–EC system was calculated to be 11.45% using the equation \( \eta_{\text{SC}} = J_{\text{op}} \times V_{\text{ph}} \div P_{\text{in}} \), where \( J_{\text{op}} \) is the operation photocurrent density, \( V_{\text{ph}} \) is the thermodynamic voltage required for electrolysis (i.e., 0.954 V for our system and 1.23 V for the overall water electrolysis), and \( P_{\text{in}} \) is the irradiation power.\(^{[67,68]}\) Moreover, a chronoaomperometric trace of the PEC–EC system was recorded at 0 V under 1-sun illumination to evaluate its stability during photosynthesis (Figure 6c). The PEC–EC cell preserved 75% of its initial photocurrent density after 25 h of operation, and the slight decrement in photocurrent density was attributed to the consumption of iodides during IOR. However, the initial photocurrent density was almost recovered as the electrolyte was replenished after 18 h of photoelectrolysis, indicating the outstanding durability of the PEC–EC device. After electrolysis, the carbon cloth electrode was immersed in anolyte for iodine reduction reaction (IRR), whereas Co-Ni\(_3\)S\(_2\) was submerged in catholyte for OER of H-type cell. As shown in Figure S31a (Supporting Information), the LSV curve displayed that this two-electrode system required only 1.3 V to afford the current density of 5 mA cm\(^{-2}\), which is attributed to the superior IRR catalytic activity over carbon cloth as well as acceptable OER activity over Co-Ni\(_3\)S\(_2\) (Figures S31b and S16, Supporting Information). During the chronoaomperometric test with initial current density of 4 mA cm\(^{-2}\), the current value decreased with the extending electrolysis time because the IRR consumes iodine (Figure S31c, Supporting Information). After 2 h of electrolysis, the light-yellow solution became transparent owing to the reduction of iodine into iodide (Figure S31d, Supporting Information), representing that the electrolyte for IOR could be recyclable. Furthermore, our Co-Ni\(_3\)S\(_2\)/PSK photoanode was devised as an artificial leaf to mimic photosynthesis of solar fuel when submerged in a one-compartment electrolyte containing 0.5 M KI dissolved in sea water (pH\( \approx 8\)). As seen in Figure 6d, the Co-Ni\(_3\)S\(_2\) catalyst was deposited on the boundary of the Ni foil to avoid the complete burial of active sites beneath the device. Meanwhile, the HER catalyst was prepared by sputtering platinum (Pt) particles on carbon cloth (Pt/CC) to maximize the catalytic surface area, and the Pt/CC was attached to the bottom electrode (FTO) of the Co-Ni\(_3\)S\(_2\)/PSK photoanode using silver paste. The artificial leaf device was entirely encapsulated by epoxy as a protective layer, except for the active areas for photoelectrolysis and the back side of FTO through which light was illuminated (Figure S32a, Supporting Information). This autonomous device can enable unassisted solar fuel production directly in the absence of external wiring, offering a distinct advantage for diverse applications owing to its mobility, adaptable scalability, and straightforward design.\(^{[69]}\) To confirm the feasibility of our artificial leaf enabling HER as well as IOR in sea water, the PEC IOR activity of the Co-Ni\(_3\)S\(_2\)/PSK photoanode was evaluated in 0.5 M KI dissolved in natural sea water using a three-electrode system under 1-sun irradiation (Figure S33a, Supporting Information). Interestingly, the Co-Ni\(_3\)S\(_2\)/PSK photoanode delivered a photocurrent density of 22.4 mA cm\(^{-2}\) at 0.4 V \( \text{RHE} \) and an onset potential of \(-0.14\) V \( \text{RHE} \), which was less than the thermodynamic HER potential (0 V \( \text{RHE} \)), evidencing the viability of our artificial photosynthetic system even in sea water. In addition to Co-Ni\(_3\)S\(_2\)/PSK photoanode, the Co-Ni\(_3\)S\(_2\) catalyst exhibited onset potential difference between KPI-based electrolyte and seawater-based electrolyte (Figure S33b, Supporting Information), due to the difference in pH of electrolyte. The seawater-based electrolyte exhibited pH value of 8, which was larger than KPI-based electrolyte (\( \approx 6.5\)). Since the IOR is pH-independent on NHE scale and pH-dependent on RHE scale, the onset potentials observed for both the Co-Ni\(_3\)S\(_2\)/PSK photoanode and Co-Ni\(_3\)S\(_2\) in two distinct electrolytes could be the same at NHE scale (Figure S33c and d, Supporting Information). In contrast, the difference in onset potentials of (photo)electrode at RHE scale was \( \approx 90\) mV based on the equation 1. Furthermore, the Co-Ni\(_3\)S\(_2\)/PSK photoanode displayed excellent durability even in natural sea water-based electrolyte, retaining \( \approx 85\% \) of its initial photocurrent density for 20 h (Figure S34, Supporting Information). Subsequently, Figure S32b and Video S1 (Supporting Information) reveal that when this stand-alone artificial leaf was operated in natural sea water, hydrogen bubbles were
Figure 6. a) Schematic of the PEC–EC tandem configuration. b) LSV curve and c) operational stability of the PEC–EC tandem configuration without applied bias under 1-sun illumination. d) Schematic configuration of the wireless artificial leaf.

generated at Pt/CC under outdoor sunlight. Generally, sea water-based OER is driven by adding potassium hydroxide (KOH) in natural sea water. However, when the KOH is dissolved in natural seawater, the precipitates such as CaCO$_3$ and Mg(OH)$_2$ likely form.$^{[70,71]}$ The obtained precipitates should be filtered to operate OER in natural seawater, which induces additional procedure. On the other hand, the KI could be dissolved in sea water without precipitates, thus the IOR could be driven without filtering process, suggesting better compatibility between natural sea water and IOR. Our findings clearly open a new pathway for practical solar fuel production enabled by artificial leaves using an ETL-passivated perovskite photoanode combined with IOR and HER catalysts.

3. Conclusion

In summary, we demonstrated a high-performance unbiased photosynthesis process using an interface-engineered perovskite-based photoanode combined with an IOR catalyst. The MPA treatment effectively mitigated inherent defects in the ETL as well as modified the band alignment at the ETL/perovskite interface, improving the optoelectrical characteristics of the perovskite photoanode. Then, a Co-doped Ni$_3$S$_2$ catalyst layer was applied to the perovskite photoanode to deliver efficient PEC IOR performance. The influence of Co doping on Ni$_3$S$_2$ was confirmed by experimental analysis and computational calculation. The Co-Ni$_3$S$_2$ catalyst exhibited a small anodic potential
of 0.97 V_{RHET} to achieve an iodide oxidation current density of 10 mA cm⁻² in neutral electrolyte, with a remarkable stability of 150 h without any loss. The perovskite photoanode, integrated with the defect-passivated ETL, and efficient IOR catalyst, yielded a saturated photocurrent density of 22.4 mA cm⁻² at 0.3 V_{RHE} with a notably small onset potential of ~0.2 V_{RHE} as well as an ultrastable lifetime of 225 h. Moreover, the unassisted solar-driven hydrogen generation PEC–EC system composed of the perovskite photoanode and Pt coil achieved a high SCC efficiency of 11.45%. Subsequently, solar-driven hydrogen generation enabled by a wireless artificial leaf was demonstrated for the first time in natural sea water by utilizing the perovskite photoanode, which opens up potential avenues for practical applications.

4. Experimental Section

Materials: Urea (ACS reagent, 99.0–100.5%), tin (II) chloride dihydrate (SnCl₂·2H₂O, ACS reagent, 98%), thioglycolic acid (TGA, 99%), cesium iodide (CsI, 99.999%, trace metal basis), Ni foil, lead bromide (PbBr₂, 99.999%), 2,2′,7,7′-tetrakis[N,N-dimethoxymethyl]amine–9,9′-spirobifluorene (spiro-OMeTAD), lithium salt of bis(trifluoromethane)sulfonimide (Li-TFSI, 99.95%), methylammonium iodide (MAI), cobalt(III) chloride hexahydrate (CoCl₂·6H₂O, ACS reagent, 98%), thiourea (NH₂)₂CS, 99%), and 4-tert-butylpyridine (TBP, 96%) were purchased from Sigma-Aldrich (USA). Isopropyl alcohol (IPA, 99.5%), hydrochloric acid (HCl, extra pure grade), and ethylacetate (EA, 99.5%) were purchased from Duksan General Science (Korea). Lead (II) iodide (PbI₂, metal basis, 99.9%), methylammonium chloride (MACl, >99.9%), methylammonium iodide (MAI), and formamidinium iodide (FAI, >99.9%) were purchased from Greatcell Solar Materials (Australia). Natural sea water was collected from Jinhae bay located in the South Sea of Republic Korea.

Preparation of ETL: Tin (II) chloride dihydrate (550 mg) and urea (2.5 g) were dissolved in 200 mL of deionized (DI) water. Under ambient atmosphere, 2.5 mL of HCl was introduced into the solution, followed by the addition of 50 μL of TGA. FTO substrates (4 × 4 cm) were cleaned by sonication with acetone, DI water, and IPA for 15 min each. The FTO substrate was then immersed in the as-prepared solution and bathed at 1.5 h at 90 °C. Afterward, the substrate was washed in the sonicator with DI water and IPA for 10 min each, followed by annealing at 170 °C for 60 min. To fabricate MPA-SnO₂, 10 mg of 4-methoxyphenethylamine (Sigma–Aldrich) was dissolved in 1 mL of dimethylformamide (DMF). The MPA solution was spin-coated on a bare SnO₂ substrate at 5000 rpm for 30 s, followed by annealing by 100 °C for 10 min.

Fabrication of PSK Photoanode: The perovskite (FAPbI₃)₀.₉₅(MAPbBr₃)₀.₀₅ solution was prepared by mixing FAI (481.516 mg), MACI (67.52 mg), MABr (16.5 mg), PbBr₂ (1410.7 mg), PbBr₂ (54.1 mg), and CsI (36.4 mg) in a mixture of dimethyl sulfoxide (0.48 mL) and DMF (1.92 mL) under continuous stirring. The MPA-SnO₂ and bare SnO₂ substrates were exposed to oxygen plasma for 17 min, by sequential sonication with acetone, DI water, and IPA for 15 min each. The FTO substrate was then immersed in the as-prepared solution and bathed at 1.5 h at 90 °C. Afterward, the substrate was washed in the sonicator with DI water and IPA for 10 min each, followed by annealing at 170 °C for 60 min. To fabricate MPA-SnO₂, 10 mg of 4-methoxyphenethylamine (Sigma–Aldrich) was dissolved in 1 mL of dimethylformamide (DMF). The MPA solution was spin-coated on a bare SnO₂ substrate at 5000 rpm for 30 s, followed by annealing by 100 °C for 10 min. Au was deposited as a top electrode on the HTL by thermal evaporation. Carbon black powder (Jetien) and epoxy (Henkel, LOCTITE 120 HP) was spread on the Au electrode, followed by the attachment of Ni foil (0.125 mm, Sigma–Aldrich). Before attachment, the Ni foil was washed using a sonicator with acetone and IPA for 10 min, respectively. After attaching the Ni foil, the epoxy resin was applied to encapsulate the PSK photoanode, preventing water permeation except for the active region. Subsequently, the Co-Ni₃S₂ electrode was attached to the Ni foil with silver paste (Elcoat). The entire process of fabricating PSK photoanode was performed in a controlled humidity environment (RH < 20%).

Preparation of Ni₃S₂-Based Electrodes: The nickel foil was cleaned using sonification with DI water, ethanol, and acetone for 15 min each. The 0.1045 g of thiourea was dissolved in 30 mL DI water, and the varying amount (0.237, 47.5, 71.1, and 95.0 mg) of CoCl₂·6H₂O were added, responding to undoped Ni₃S₂, Co₀.₄Ni₃S₂, Co₀.₂Ni₃S₂, Co₀.₁Ni₃S₂, and Co₀ Ni₃S₂ electrodes, respectively. The precursor solution was sonicated for 15 min. The hydrothermal reaction was carried out at 140 °C for 12 h by employing a 100 mL Teflon-lined stainless-steel autoclave in which the cleaned nickel foil was immersed in the precursor solution. The resultant electrodes were washed by DI water several times for removal of the residual reactants and then dried at 60 °C for 12 h in air.

Characterization of Optical, Structural, and Electrical Properties: Surface images were obtained by field-emission SEM (JSM-7001F, JEOL, Japan). Steady-state PL spectra of perovskite films were analyzed after excitation at 532 nm (MAPLE-II, Dongwoong Optron, Korea). TRPL analysis was performed at a laser excitation wavelength of 371 nm using a fluorescence spectrophotometer (Fluoromax-4, Horiba, Japan) and the emission wavelength for TRPL measurement was determined to be 780 nm. NX-10 AFM (Park Systems, Korea) was employed to analyze the topology and conductivity of bare SnO₂ and MPA-SnO₂ under the contact mode. The crystalline structures of the PSK layers as a function of MPA treatment on bare SnO₂ substrate and Ni₃S₂-based electrodes were investigated through XRD analysis (MiniFlex 600, Rigaku, Tokyo, Japan) using Cu Kα radiation (λ = 0.15406 nm). In addition, XPS (K-alpha, Thermo Scientific Inc., UK) was performed to observe the surface chemical state. All XPS spectra were calibrated with the C 1s peak (284.8 eV). A Gaussian peak function was utilized to observe the fitted values. The ultraviolet photoelectron spectroscopy (Ultra DLD and Axis-NOVA, UK) was performed under He I radiation (21.2 eV) to investigate the work function of each sample. The secondary-electron cut-off region (E_{cut-off}) was calculated by linearly extrapolating the binding energy edge. The work function (W_F) of each sample was calculated as follows:

\[ W_F = E_{cut-off} - 21.21 \text{ eV (under He I radiation)} \]  

The valence-band edge (E_{VBM}) represents the difference between E_{VBM} and Fermi level (E_F). The definite valence band maximum (VBM) level of the samples was obtained using the E_{edge} values based on the following equation:

\[ E_{VBM} = E_{edge} + E_F \]
TPC measurements of bare SnO₂ and MPA-SnO₂ PSC were performed using an electrochemical workstation (Zennium, Zahner, Germany) and a potentiostat (PP211, Zahner, Germany).

( Photo) Electrochemical Measurements: The catalytic area ranged from 0.06 to 0.2 cm² and the exposed area of the PSK photoelectrodes was controlled to be identical with catalytic area using aperture mask. The electrolyte was magnetically stirred at 400 rpm during (photo)electrochemical measurements. The LSV and chronoamperometry measurements of the Ni₃S₂-based electrodes and PSK-based photoanodes were conducted under dark and 1-sun illumination (AM 1.5G) using a three-electrode system comprising Ag/AgCl/KCl (saturated) as the reference electrode and Pt coil as the counter electrode. For the LSV measurements of Ni₃S₂-based electrodes, all potentials were compensated with IR correction. Moreover, in all (photo)electrochemical measurements, the applied potential values were converted into RHE value using the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.05916 \times pH + 0.197$$  \hspace{1cm} (7)

Further, EIS was measured using a potentiostat with a frequency analyzer (1260, Solartron, Leicester, UK). The polarization and series resistances of the Ni₃S₂-based electrodes were determined in the frequency range of 100 kHz–0.1 Hz with an alternating-current amplitude of 10 mV. The Cₚ values were investigated using CV curves to determine the ECSA according to the following equation:

$$C_p = \frac{J_0 - J_1}{2 \times v} = \frac{J_0 + |J_1|}{2 \times v} = \frac{0.5 \times |\Delta J|}{v}$$  \hspace{1cm} (8)

In which, $J_0$ and $J_1$ are the anodic and cathode voltammetric current density recorded at open circuit potential, respectively, and $v$ was the scan rate. IPCE measurement of the Co-Ni₃S₂/PSK photoanode was performed using an electrochemical workstation (Zennium, Zahner, Germany), potentiostat (PP211, Zahner, Germany) and a monochromatic light source (TLS03, Zahner). Iodometric titration was employed to evaluate the quantity of iodine produced at the Co-Ni₃S₂/PSK photoanode.

Gas chromatography (6500GC system, YL Instrument, Anyang, Korea) was conducted using a molecular sieve column and pulsed discharge detector to quantify the H₂ evolution. Rubber bulkheads and a para film were employed for completely sealing the PEC device to prevent H₂ gas leakage. The iodometric titration and gas chromatography were performed using an H-type cell, and a Nafion N-117 membrane was used to separate the Co-Ni₃S₂/PSK photoanode (working electrode) as well as reference electrode in KPi buffer electrolyte with KI from the counter electrode in pure KPi electrolyte. The iodometric titration method was conducted as follows. The quantity of iodine in the electrolyte was titrated by 10 mmol solution of sodium thiosulfate (Na₂S₂O₃), through following reaction:

$$2Na_2S_2O_3 + 2I^- + 2Na^2+ + Na_2S_2O_4$$  \hspace{1cm} (9)

Before the titration, 5 µL of 1.96% starch solution was introduced into the electrolyte to serve as an indicator, inducing the formation of a dark blue iodine-starch complex. The end of the titration was marked by the transition of the electrolyte from a dark blue to transparent state. The same transition of the electrolyte from an iodine oxidation, perovskite photoanode, unbiased hydrogen production reaction:

$$I_2 + 2Na_2S_2O_3 \rightarrow 2I^- + 2Na^2+ + Na_2S_2O_4$$

for IOR was determined as $AG = AG_{ads} + AG_{ZPE} - T \Delta S$, where $AG_{ads}$ represents the iodine adsorption energy and $AG_{ZPE}$ and $\Delta S$ denote the zero-point energy and entropy difference between the free and adsorbed states, respectively. In the IOR process involving \(1^- \rightarrow 1/2 I_2 + e^-\), iodine binds to the surface of Ni₃S₂, and the $AG$ for iodide adsorption serves as a descriptor of IOR activity. \[8\]

Supporting Information

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

Acknowledgements

J.Y. and Y.S.P. contributed equally to this work. This research was supported by the National R&D Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (No. 2021R1A3B1068920 and 2021M3H4A103049662). This research was also supported by the Yonsei Signature Research Cluster Program of 2021 (2021-22-0002) and the Yonsei Fellowship, funded by Lee Youn Jae.

Conflict of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

interface engineering, interface engineering, iodide oxidation, perovskite photoanode, unbiased hydrogen production

Received: March 7, 2024
Revised: May 9, 2024
Published online:


