Multifunctional Coatings from Scalable Single Source Precursor Chemistry in Tandem Photoelectrochemical Water Splitting

Yi-Hsuan Lai, David W. Palm, and Erwin Reisner*

The straightforward and inexpensive fabrication of stabilized and activated photoelectrodes for application to tandem photoelectrochemical (PEC) water splitting is reported. Semiconductors such as Si, WO$_3$, and BiVO$_4$ can be coated with a composite layer formed upon hydrolytic decomposition of heterobimetallic single source precursors (SSPs) based on Ti and Ni, or Ti and Co in a simple single-step process under ambient conditions. The resulting 3d-transition metal oxide composite films are multifunctional, as they protect the semiconductor electrode from corrosion with an amorphous TiO$_2$ coating and act as bifunctional electrocatalysts for H$_2$ and O$_2$ evolution based on catalytic Ni or Co species. Thus, this approach enables the use of the same precursors for both photoelectrodes in tandem PEC water splitting, and SSP chemistry is thereby established as a highly versatile low-cost approach to protect and activate photoelectrodes. In an optimized system, SSP coating of a Si photocathode and a BiVO$_4$ photoanode resulted in a benchmark noble metal-free dual-photoelectrode tandem PEC cell for overall solar water splitting with an applied bias solar-to-hydrogen conversion efficiency of 0.59% and a half-life photostability of 5 h.

1. Introduction

Solar-driven water splitting is an attractive technological concept for the generation of sustainable H$_2$ fuel from sunlight and water.[1] A photoelectrochemical (PEC) cell is a promising device for fulfilling this purpose because its capital cost may potentially be lower than that of an electrolyzer wired to photovoltaic (PV) modules, and it has an attractive theoretical efficiency.[2] The upper limit efficiency of a tandem PEC cell with a pair of semiconductors having band gaps of 1.0 and 1.6 eV is close to 30%,[3] whereas only 13% is achievable for a single light absorber PEC cell consisting of a semiconductor with a band gap of 2.2 eV.[2a]

Several designs of tandem PEC cells are currently under investigation.[4] For example, tandem cells that use a single dual-absorbing photoelectrode paired with an expensive platinum counter electrode,[5] or PVs integrated with a photoelectrode are widely studied.[6a–c] In contrast, studies of tandem PEC cells that pair a photoanode with a photocathode are still limited (Figure 1).[6] Toward this goal, immense efforts have been devoted to optimize the performance of individual photoelectrodes by interfacing them with protection layers to enhance photostability and by integrating electrocatalysts for more efficient fuel formation.[1a,7] In addition, major challenges arise from the incompatibility between photoanode and photocathode materials, electrolyte solutions, integrated catalysts, and/or other elements.[1a,2a] A simple, cost-effective, and universal process to protect and activate the photoelectrodes and make them compatible with each other would therefore be very beneficial.

Protection of promising but photo-unstable electrode materials with a stable and conducting layer such as amorphous TiO$_2$ is an attractive approach to enhance their lifetime during operation in a PEC cell. However, these protection layers are typically prepared by costly atomic layer deposition (ALD)[7d,8] or sputtering technologies,[9] which are challenging to scale up. In order to enhance photocatalytic performance, electrocatalysts are integrated onto semiconductor electrodes that exhibit low photocurrent densities.[7a,b] Bifunctional water splitting electrocatalysts can promote both the hydrogen and oxygen evolution reactions, and are an interesting approach for minimizing the complexity and cost of integrated water splitting systems.[10] However, such bifunctional catalysts have only been reported for water electrolysis, and their preparation has required electrodeposition and chemical synthesis, which have thus far prevented their simple integration in a PEC system.

Solution processed single source precursor (SSP) chemistry is an attractive approach for preparing multifunctional materials on a large scale, as it bypasses the need for expensive equipment and processing.[11] A SSP contains all of the required elements for a desired composite material, allowing for its synthesis in a simple, one-step procedure. In addition, the material prepared from an SSP can comprise novel composite phases and oxidation states, which might be difficult to achieve with conventional synthetic routes.[11a,e]
Herein, we report on a highly versatile and scalable SSP approach for preparing a composite film on photoelectrodes. This composite is multifunctional, serving three main purposes: it protects the photoelectrode from corrosion and can act as both a hydrogen evolution catalyst (HEC) and an oxygen evolution catalyst (OEC) in the same neutral-alkaline solution. Thus, individual photoelectrodes coated with the SSPs can also be arbitrarily combined in tandem PEC cells. The SSPs employed in this study are [Ti₂(OEt)₉(NiCl)]₂ (TiNiSSP) and [TiO₂(OEt)₁₃(CoCl)] (TiCoSSP) (Figure 2). TiNiSSP and TiCoSSP were selected first because their hydrolysis forms amorphous TiO₂, which is inexpensive and the most widely used protective coating on photoelectrodes that suffer from severe instability. Furthermore, decomposition of the SSPs will form Ni⁷⁺, Co⁺, and Co⁶⁺ species, which are among the best noble metal-free HECs and OECs and can show bifunctionality for water splitting catalysis. In addition, TiNiSSP and TiCoSSP can be easily synthesized by a single mid-temperature solvothermal step, with respectable yield. We demonstrate that the SSPs can be deposited onto Si, WO₃, and BiVO₄, where they are activated in situ to protect and catalytically activate the semiconductors for both half-reactions in PEC water splitting. Optimized SSP-modified photoelectrodes allowed for the assembly of a benchmark tandem water splitting cell.

2. Results and Discussion

2.1. Electrochemical Characterization

The simple coating of the SSPs (TiNiSSP and TiCoSSP) onto conducting substrates through room temperature deposition allows for the formation of bifunctional composite materials active as HEC and OEC in a pH 9.2 potassium borate (B₃) solution (Figure 3). Hydrolytic decomposition of TiNiSSP (2 × 20 µL, 5 × 10⁻¹³ m in dry toluene) on a fluoride-doped tin oxide (FTO)-coated glass substrate (1 cm²) has been previously shown to result in an amorphous Ti- and Ni-containing precursor film (FTO|TiNiₚ)⁷⁺. Under anodic conditions, a NiO₃ OEC embedded in a TiO₂ matrix was formed in situ (TiNioEC).⁸⁺ whereas an in situ cathodic activation process of the TiNiₚ film gave a Ni-based HEC that consists of metallic Ni embedded in an amorphous NiO/Ni(OH)₂ and TiO₂ matrix (TiNioEC, Figure 3a). FTO|TiNiOEC and FTO|TiNiₚ show a catalytic onset potential (E₉₀⁺) of ≈1.7 and −0.1 V versus the reversible hydrogen electrode (vs RHE) for O₂ and H₂ evolution, respectively, and Faradaic efficiencies (FEs) of more than 90% for both processes (Table 1).

Drop-casting of TiCoSSP (2 × 20 µL, 10 × 10⁻¹³ m in dry toluene) on an FTO-coated glass substrate (1 cm²) resulted in an amorphous precursor film on FTO (FTO| TiCoₚ). TiCoₚ is a mixture of agglomerated amorphous particles of TiO₂ and CoO/Co(OH)₂, which was confirmed by scanning electron microscopy (SEM), powder X-ray diffraction (p-XRD), and X-ray photoelectron spectroscopy (XPS; Figures S1 and S2, Supporting Information). Under an anodic potential, TiCoₚ converts in situ into TiCoOEC, which contains the well-known CoO₂ OEC in B₃ solution (Figure 3a and Figure S3, Supporting Information). FTO|TiCoOEC electro-oxidizes water to O₂ with an onset potential of approximately E₉₀⁺ ≈ 1.6 V versus RHE (Figure 3b) and a FE of 88% at an applied potential (Eappl) of 2.0 V versus RHE (Table 1 and Figure S3, Supporting Information). TiCoOEC forms upon a cathodic activation of TiCoₚ at Eappl of −0.6 V versus RHE for

2.2. Photocatalytic Activity

The three-component composite TiNiCoSSP/FTO water splitting cell (FTO|TiNiCo pre |TiNiOEC|TiCoOEC) was assembled in a pH 9.2 potassium borate (B₃) solution (100 mL) with 0.1 M potassium phosphate buffer and 100 ppm Triton X-100 surfactant under simulated solar irradiation (100 mW cm⁻², AM 1.5G). Table 1 summarizes key performance parameters for electro- and photocatalytic H₂ and O₂ production and the corresponding FE in a pH 9.2 B₃ (0.1 m) electrolyte solution at room temperature.

Table 1. Summary of key performance parameters for electro- and photocatalytic H₂ and O₂ production and the corresponding FE in a pH 9.2 B₃ (0.1 m) electrolyte solution at room temperature.

| Eappl [V vs RHE] | O₂ or H₂ [µmol h⁻¹ cm⁻²] | FE [%] | ref. |
|-----------------|--------------------------|-------|-----|
| FTO|TiNiOEC | 2.0 | 9.8 | 90 | [11c] |
| FTO|NiHEC | −0.6 | 96 | 97 | [11a] |
| FTO|TiCoOEC | 2.0 | 14.3 | 88 | This work |
| FTO|TiCoOEC | −0.6 | 73 | 92 | This work |
| WO₃ | 1.23 | 0.7 | 56 | [11c] |
| WO₃|TiNiOEC | 1.23 | 2.2 | 74 | [11c] |
| BiVO₄ | 1.23 | N/A | N/A | This work |
| BiVO₄|TiCoOEC | 1.23 | 9.2 | 78 | This work |
| p-Si | 0 | N/A | N/A | This work |
| p-Si|TiNiOEC | 0 | 74 | 100 | [11a] |

*Photoelectrodes were irradiated with a solar light simulator (100 mW cm⁻², AM 1.5G). N/A indicates that the amount of produced gas was below the limit of quantification.*
Figure 3. a) The proposed mechanism of the transformation of TiNiSSP and TiCoSSP to their respective precursor films and bifunctional water splitting catalysts. b) Cyclic voltammetry (CV) showing the anodic response of FTO|TiNiOEC and FTO|TiCoOEC for water oxidation as well as the cathodic response of FTO|TiNiHEC and FTO|TiCoHEC for proton reduction. Bare FTO is also shown. All CV scans were performed at room temperature in an aqueous electrolyte solution (0.1 M B, 0.1 M K2SO4, pH 9.2) at a scan rate of 50 mV s⁻¹. FTO|TiNiOEC and FTO|TiCoOEC exhibit an oxidation wave of Ni³⁺/Ni²⁺ and Co³⁺/Co²⁺ at approximately Em = 1.58 and 1.41 V versus RHE, respectively. 

The current–voltage characteristics and the near-quantitative FE confirm that both TiNiSSP and TiCoSSP act as precursors of HECs and OECs and are therefore rare examples of bifunctional water splitting electrocatalysts. Although the catalytic onset overpotential of these electrocatalysts is somewhat higher than that of other benchmark electrocatalysts, the photocurrent of a photoelectrode during irradiation is not necessarily limited by the nonideal response of the composite electrocatalysts. Figure 3b indicates the relevant minority carrier band positions of the semiconductors used in this study, illustrating that a catalyst with a very small overpotential requirement is not necessary for the HEC and OEC to function efficiently in such a PEC system. With respect to the standard potential (E⁰) of the appropriate half-reaction, an overpotential (η) of 0.6 V is available for H₂ evolution on p-Si and an η of 1.8 and 1.3 V for O₂ generation on WO₃ and BiVO₄, respectively. Furthermore, BiVO₄ and WO₃ can only provide theoretical maximum photocurrent densities of 7 and 5 mA cm⁻², respectively, suggesting that the photocurrent will be limited by light absorption and charge separation of the photoanode rather than electrocatalysis by TiNiOEC and TiCoOEC.

2.2. SSP-Coated Photoelectrodes and Performance

Bifunctionality in water splitting catalysis has only been demonstrated in water electrolysis to date. Here, we explore the utility of composite films from TiNiSSP and TiCoSSP to form protective and bifunctional catalyst layers on state-of-the-art semiconductors in PEC water splitting. While the electrocatalytic
activities of the TiNi and TiCo composite films have already been evaluated by electrochemical methods (Figure 3b and Table 1), the coating’s success on a semiconductor also strongly depends on the formation of a good interface between the composite and the photoelectrode. A key advantage of our solution-based SSP approach is its simple application to a wide range of substrates by approaches like spin-coating, drop-casting, dip-coating, or inkjet spraying, followed by hydrolytic decomposition under ambient conditions to form a well-interfaced and multifunctional composite layer.

p-Si has been selected as photocathode due to its near-ideal small band gap of 1.1 eV, providing a theoretical photocurrent density of 44 mA cm⁻². WO₃ and BiVO₄ are chosen as state-of-the-art photoanodes having band gaps of 2.6 and 2.4 eV, respectively, thus providing respectable photocurrents under solar light irradiation. Additionally, thin films of these n-type semiconductors are easily prepared without requiring arduous solar light irradiation. Furthermore, thin films of these n-type semiconductors are easily prepared without requiring arduous procedures (i.e., no high-temperature annealing above 600 °C), and exhibit promising water oxidation activity. 

For use in PEC hydrogen evolution, the surface of p-Si must be coated with a protective layer and a HER in order to prevent quenching of photocactivity due to the rapid formation of SiO₂, and to overcome the kinetic barriers for proton reduction. We have previously demonstrated that TiNi(SSP acts as an SSP to form a protective TiO₂ layer and a Ni-based HER on p-Si. A p-Si|TiNiHESC electrode was prepared by drop-casting a TiNiSSP solution (8 × 30 µL cm⁻², 2.5 × 10⁻³ M in dry toluene) onto a planar p-Si electrode (0.5 cm²) followed by cathodic in situ activation at Eₚₐₚ pH = 0 V versus RHE under solar light irradiation in a pH 9.2 B₃ solution (Figure S5, Supporting Information).

Figure 4. a) Linear sweep voltammetry (LSV) scans of p-Si|TiNiHESC directly irradiated with chopped light (black trace) and with chopped irradiation filtered by a nanoBiVO₄|TiCoOEC electrode (olive). The photoresponse of nanoWO₃|TiNiOEC (blue) and nanoBiVO₄|TiCoOEC (red) is also shown and all LSVs were recorded in a pH 9.2 Bi electrolyte solution. Inset magnifies the curve near 0.3 V. b) LSV scans of nanoBiVO₄|TiCoOEC for water oxidation, and nanoBiVO₄ for sulfite oxidation. All measurements were performed in an aqueous pH 9.2 electrolyte solution (0.1 M B₃ and 0.1 M K₂SO₃ for water oxidation; 0.1 M B₃ and 0.1 M Na₂SO₃ for sulfite oxidation) under chopped irradiation with a scan rate of 5 mV s⁻¹. An Ag/AgCl/KCl electrode was employed as the reference electrode, and a Pt foil as the counter electrode; all experiments were conducted at room temperature and irradiation was provided by a solar light simulator (100 mW cm⁻², AM 1.5G).
and an NiO\textsubscript{x} OEC on WO\textsubscript{3}.\textsuperscript{[11c]} Illuminated nanoWO\textsubscript{3}|TiNi OEC shows an $E_{\text{cat}}$ of $\approx$0.6 V, a saturation photocurrent density of 0.6 mA cm\textsuperscript{−2} at 1.23 V versus RHE and a FE of 74\% at $E_{\text{appl}} = 1.23$ V versus RHE in aqueous pH 9.2 B\textsubscript{i} solution (Table 1, Figure 4a).\textsuperscript{[11c]} A TiCoO\textsubscript{3} layered nanoWO\textsubscript{3} electrode (nanoWO\textsubscript{3}|TiCoO\textsubscript{3}) was also assembled by the same method, but showed slightly poorer performance than nanoWO\textsubscript{3}|TiNi OEC (Figure S9, Supporting Information); accordingly, nanoWO\textsubscript{3}|TiNi OEC was used in the following tandem cell study.

In the absence of TiNi coating, nanoWO\textsubscript{3} lost 50\% of its initial photocurrent within 1 h in pH 9.2 B\textsubscript{i} solution. In contrast, nanoWO\textsubscript{3}|TiNiOEC shows a half-life time of 4 h under the same conditions, demonstrating the composite film's role as protection layer.\textsuperscript{[11c]} In addition, the TiNi coating enhances the photocurrents of nanoWO\textsubscript{3} in the low bias region ($<1.15$ V vs RHE, Figure S9, Supporting Information). Thus, nanoWO\textsubscript{3}|TiNiOEC serves as a suitable photoanode to pair with p-Si|TiNi HEC in pH 9.2 solution in tandem PEC studies. We note that the TiNiOEC coating likely does not fully prevent WO\textsubscript{3} from direct contact with alkaline solution, contributing to the deactivation of nanoWO\textsubscript{3}|TiNiOEC on longer time scales. We also point out that the lifetime of our protected photoelectrodes is less than that of the top-performing TiO\textsubscript{2} passivated electrodes prepared by ALD technique,\textsuperscript{[7d]} which yields denser and more conformal protective coatings compared to the sol–gel processed SSP chemistry employed here. With further studies, including tuning the molecular ligand and applying a self-assembly strategy to immobilize a monolayer of the SSP onto the electrode before decomposition, a more conformal coating may be achieved and provide better surface protection functions.

BiVO\textsubscript{4} has a smaller band gap and thus a higher theoretical photocurrent density than WO\textsubscript{3}.$^{[2c, 7a, 20]}$ BiVO\textsubscript{4} also has a more negative conduction band potential ($E_{\text{CB}} = +0.1$ V vs RHE) than WO\textsubscript{3} ($E_{\text{CB}} = +0.4$ V vs RHE), which should provide a higher photovoltage and operating photocurrent when paired with p-Si in a tandem PEC cell. Key drawbacks of BiVO\textsubscript{4} are poor carrier mobility and slow water oxidation kinetics, though near-complete suppression of surface recombination by electrodeposited amorphous CoO\textsubscript{x} on BiVO\textsubscript{4} has been recently demonstrated.$^{[4d]}$ Thus, we were particularly interested in the effect of TiCoO\textsubscript{3} on BiVO\textsubscript{4}.

Monoclinic scheelite BiVO\textsubscript{4} was synthesized by a combined electrochemical deposition/metal-organic decomposition synthesis as reported$^{[2a]}$ and characterized by SEM and p-XRD (Figure 5d,e and Figure S10, Supporting Information); the

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**Figure 5.** SEM images of: a,b) nanoWO\textsubscript{3}, c) nanoWO\textsubscript{3}|TiNiOEC; d,e) nanoBiVO\textsubscript{4}, and f) nanoBiVO\textsubscript{4}|TiCoOEC.
nanoporous structure (nanoBiVO₄) prepared in this manner has been shown to improve performance, purportedly by reducing the required hole diffusion length and enhancing the catalytic surface area. NanoBiVO₄/TiCoOEC was prepared by spin-coating a TiCoOSSP solution (4 × 20 μL cm⁻², 5 × 10⁻³ M in dry toluene) onto a nanoBiVO₄ electrode. No drastic surface morphology change was observed, but the nanoBiVO₄ appeared to be decorated with an agglomerated Ti- and Co-containing film (Figure 5f). NanoBiVO₄/TiCoOEC exhibits an Ecat = 0.2 V versus RHE and j = 1.8 mA cm⁻² at Eappl = 1.23 V versus RHE for water oxidation in pH 9.2 B₃ solution during irradiation (Figure 4b). Modification of nanoBiVO₄ photoanode surfaces with TiCoOEC yielded a significant cathodic shift in Ecat and a substantial enhancement of the photocurrent compared to bare nanoBiVO₄ (Figure 4b and Figure S11, Supporting Information). Comparing this composite electrode performance to that of bare nanoBiVO₄ in PEC experiments with Na₂SO₄ as a hole scavenger reveals that interfacing TiCoOEC with nanoBiVO₄ almost completely eliminates losses due to surface electron–hole recombination. A FE of 78% was observed at Eappl = 1.23 V versus RHE for nanoBiVO₄/TiCoOEC (Table 1 and Figure S12, Supporting Information). A TiN₀EC catalytic film also helps suppress the surface charge recombination of BiVO₄, but is less effective than TiCoOEC (Figure 4b).

The catalytic performance of the TiCoOEC composite layer on nanoBiVO₄ appears to compare favorably to that of a recently reported dual-layer FeOOH|NiOOH OEC cocatalyst, in which surface electron–hole recombination is not completely suppressed.[24] NanoBiVO₄/TiCoOEC also functions well in a neutral Pⱼ solution (0.5 M, pH 7) and shows similar performance compared to nanoBiVO₄|CoOₓ-Pⱼ, which was prepared by photo-assisted deposition of CoOₓ on a nanoBiVO₄ electrode from a Pⱼ buffer solution containing 0.5 × 10⁻³ M Co(NO₃)₂ (Figure S13, Supporting Information).[4] However, compared to this (photo)electrodeposition method, the SSP approach reported here offers a better metal-atom efficiency to produce the layer and a higher potential for large-scale production of CoOₓ OECs by low-temperature inkjet spraying or roll-to-roll processing (i.e., for conductive polymer substrates). The dissolution of a thin CoOₓ layer in the electrolyte solution during PEC measurements has been recently demonstrated[22] and might be the reason that TiCoOEC shows negligible effect on the stability of nanoBiVO₄.

2.3. Tandem PEC Cells for Overall Solar Water Splitting

Developing a PEC water splitting device that operates in a near pH-neutral environment is desirable in order to extend the range of potential light absorber and catalyst pairs to those that are not stable under strongly acidic and alkaline conditions.[14a] Additionally, operating at moderate pH allows for the use of natural water resources (including sea water)[23] and avoids the handling of corrosive solutions. The mass transport limitations imposed by the lack of H⁺ and OH⁻ ions in these conditions can be overcome by adding supporting electrolyte and by employing circulating electrolyte systems for the forced convection of ionic species.[24] With these considerations in mind, our composite photoelectrode arrays were employed in neutral-alkaline conditions, minimizing the mass-transport limitations without compromising much photoelectrode performance.

The tandem PEC cells were subsequently assembled by pairing p-Si[TiNiHEC with nanoWO₃TiNiOEC (PEC cell I) and with nanoBiVO₄|TiCoOEC (PEC cell II) for overall solar-driven (100 mW cm⁻², AM 1.5G) water splitting at room temperature (Figure 6). A two-compartment cell separated by a Nafion 117 membrane was used with photoelectrodes having geometric surface areas of ≈0.5 cm², in order to minimize efficiency losses due to the solution or material resistance. Since the photoanodes both have larger band gaps than p-Si, light was first absorbed by these photoanodes (nanoWO₃|TiNiOEC or nanoBiVO₄|TiCoOEC) and the attenuated light then arrived at the back photocathode (p-Si[TiNiHEC). Both cells were operated with the photocatalytic surfaces of the two electrodes facing one another, thus optimizing photoanode performance and minimizing ion transport resistances. It is worth noting that we have employed Nafion 117 in this study in order to prevent the crossover of the product gases, even though Nafion 117 is a proton conducting membrane that does not function ideally in neutral-alkaline conditions. Thus, the device efficiency might...
be improved if an appropriate alkali anion exchange membrane or glass frit separator is used.

**Figure 7** shows the photocurrent density of tandem PEC cell I and II at applied biases from 0 to 1.23 V in an aqueous Bi solution (0.1 m, pH 9.2) with K$_2$SO$_4$ (0.1 m) as supporting electrolyte. An external bias of at least 0.35 V is necessary for tandem PEC cell I to split water, which is consistent with the half-cell performance of p-Si|TiNi OEC: an $E_{\text{cat}}$ of $\approx 0.25$ V versus RHE is required for p-Si|TiNi HEC to photoreduce protons, whereas an $E_{\text{cat}}$ of 0.6 V versus RHE is needed for nanoWO$_3$|TiNi OEC to photo-oxidize water (Figure 4a). In PEC cell I, a photocurrent density of $\approx 400$ µA cm$^{-2}$ is achievable at an applied bias of 0.8 V, close to the expected required bias of 0.75 V predicted by the half-cell performance of the photoelectrodes (Figure S14, Supporting Information); additional required bias to produce this photocurrent density can be accounted for by the increased ohmic loss incurred in moving to a working two-electrode device.

In the case of PEC cell II, a spontaneous, unbiased photocurrent density of 45 ± 18 µA cm$^{-2}$ was observed (Figure 7a) as reasonably predicted from the half-cell performances of p-Si|TiNi$_{\text{HEC}}$ and nanoBiVO$_4$|TiCo$_{\text{OEC}}$ (Figure 4a). A photocurrent density of $\approx 1.0$ mA cm$^{-2}$ is achievable at an applied bias of 0.6 V in tandem PEC cell II, which is also in good agreement with the expected required bias of 0.75 V predicted by the half-cell performance of p-Si|TiNi$_{\text{HEC}}$ and nanoBiVO$_4$|TiCo$_{\text{OEC}}$, taking into account some losses in polarization due to solution resistance (Figure S15, Supporting Information).

A first indication of a PEC cell's performance can be determined by calculating the applied bias photon-to-current conversion efficiency (ABPE, Equation (1))

$$\text{ABPE} = \frac{j \times (1.23 - V_{\text{bias}})}{P_{\text{total}}} \text{AM1.5G} \quad (1)$$

In this equation, $j$ is the photocurrent density (mA cm$^{-2}$), $V_{\text{bias}}$ is the applied bias (V) to the tandem PEC cell, and $P_{\text{total}}$ is the energy flux of the illumination (mW cm$^{-2}$). A maximum ABPE of 0.19 ± 0.01% and 0.65 ± 0.04% was achieved at an applied bias of 0.8 V for PEC cell I and 0.6 V for PEC cell II, respectively (Figure 7b and Table 2).

![Figure 7](www.advenergymat.de)

**Table 2.** Solar water splitting performance of the tandem PEC cells I and II.

| Tandem PEC cell | ABPE [%] | H$_2$ FE [%] | O$_2$ FE [%] | STH [%] | AB-STH [%] |
|-----------------|---------|-------------|-------------|--------|------------|
| I               | 0.19 ± 0.01$^a$ | 99 ± 1.8$^a$ | 83 ± 11$^a$ | 0       | 0.19$^a$   |
| II              | 0.65 ± 0.04$^a$ | 91 ± 3.3$^b$ | 82 ± 5.3$^b$ | 0.05   | 0.59$^b$   |

$^a$Applied bias = 0.8 V; $^b$Applied bias = 0.6 V.

The stability and performance of the cells were subsequently studied at the applied bias where each tandem PEC cell exhibits the highest ABPE. Both tandem PEC cells exhibit respectable lifetime under continuous solar light irradiation, with a half-life time of 2 and 5 h for PEC cell I and II, respectively; tandem PEC cell II also retains 30% of its initial photocurrent after 24 h (Figure 7a, inset). To confirm that the photocurrent of the tandem PEC cell was due to water splitting, the amount of H$_2$ and O$_2$ produced was quantified in the reactor’s gaseous headspace by gas chromatography and a fluorescence oxygen probe, respectively (Figure S16, Supporting Information). During 1 h photoelectrolysis at an external bias of 0.8 V with tandem PEC cell I, a charge density of 1.0 ± 0.1 C cm$^{-2}$ passed through the external circuit with 5.0 ± 0.5 µmol cm$^{-2}$ of H$_2$ and 2.1 ± 0.4 µmol cm$^{-2}$ of O$_2$ being detected. The corresponding FEs are 99% for H$_2$ and 83% for O$_2$ (Table 2). In the case of PEC cell II, a charge density of 3.3 ± 0.2 C cm$^{-2}$ was generated, with a FE of 91% for H$_2$ (15.2 ± 0.2 µmol cm$^{-2}$) and 82% for O$_2$ (6.9 ± 0.1 µmol cm$^{-2}$) at an external bias of 0.6 V after 1 h of photoelectrolysis (Table 2). The near-quantitative FE and the H$_2$ to O$_2$ ratio of $\approx 2$ to 1 in both tandem cells confirm that the passed current arises mainly from water splitting.

The measurement of the FE allows us to calculate the true solar to fuel conversion efficiency without relying on the assumption of quantitative product formation. Thus, the “standalone” solar-to-hydrogen (STH) efficiency (Equation (2)) at zero applied bias can be calculated from the short-circuit photocurrent density ($j_{\text{SC}}$)

$$\text{STH} = \frac{j_{\text{SC}} \times (1.23) \times (\text{FE})}{P_{\text{total}}} \text{AM1.5G} \quad (2)$$

**Figure 7.** a) LSV scans in a two-electrode configuration under chopped solar light irradiation (100 mW cm$^{-2}$, AM 1.5G) with a scan rate of 5 mV s$^{-1}$ and b) the corresponding ABPE of tandem PEC cell I (i) and II (ii). Inset in (a) shows the chronoamperometric stability of tandem PEC I (i) and II (ii) recorded at external biases of 0.8 and 0.6 V, respectively.
PEC cell I did not show an unbiased photocurrent, but 45 \( \mu A \) cm\(^{-2}\) were generated by PEC cell II at zero applied bias corresponding to a STH of 0.05%.

Another meaningful energy conversion efficiency for a working PEC device is the efficiency of solar energy conversion to hydrogen fuel under applied bias conditions (AB-STH, Equation (3)).\(^\text{[3,6,25]}\)

\[
\text{AB-STH} = \left[ \frac{J \times (1.23 - V_{\text{bias}}) \times (FE)}{P_{\text{total}}} \right]_{\text{AM1.5G}}
\]

In this calculated, the applied bias is accounted for and only the stored chemical energy from solar photons contributes to the efficiency; hence, performing such an analysis can identify the applied bias at which a working device should be operated for highest efficiency solar-to-fuel conversion. Accordingly, the maximum AB-STH efficiency achieved is 0.19% (at 0.8 V) and 0.59% (at 0.6 V) for tandem PEC cell I and II, respectively.

### 2.4. Performance Comparison with State-of-the-Art Tandem PEC Cells

Several state-of-the-art tandem cells have been reported, including the “Turner cell” (a GaInP\(_{2}\) photocathode biased by an integrated GaAs PV, with a STH efficiency of 12.4%).\(^\text{[46]}\) an amorphous hydrogenated Si integrated with W doped BiVO\(_4\) (3.6%)\(^\text{[46]}\) and a dye-sensitized solar cell-biased WO\(_4\) (3.1%) or hematite (1.17%).\(^\text{[46]}\) However, these tandem PEC cells consist of one photoelectrode and one noble metal electrode, and thus are not directly comparable here. A STH efficiency of 8.2% was achieved by side-by-side irradiation of a dual-photoelectrode combination of p-InP and n-GaAs.\(^\text{[36]}\) However, this system also contains very expensive components, and both photoelectrodes were illuminated independently, which means that it is also not fully comparable to our stacked configuration tandem system.

Accordingly, the following discussion focuses on PEC cells consisting of one photoanode and one photocathode in tandem configuration.\(^\text{[3]}\) Recently reported dual photoelectrode tandem PEC cells include Cu\(_2\)O paired with WO\(_4\) (Cu\(_2\)O-WO\(_4\), AB-STH = 0.11%),\(^\text{[46]}\) Cu\(_2\)O paired with BiVO\(_4\) (Cu\(_2\)O-BiVO\(_4\), STH = 0.5% assuming quantitative FE).\(^\text{[68]}\) and amorphous Si paired with Fe\(_2\)O\(_3\) (aSi-Fe\(_2\)O\(_3\), STH = 0.91%).\(^\text{[66]}\) (Table 3). Cu\(_2\)O-BiVO\(_4\) and aSi-Fe\(_2\)O\(_3\) provide bias-free photocurrent densities of 0.32 and 0.74 \( \mu A \) cm\(^{-2}\), respectively, though the former system employed expensive ALD techniques and the latter used a costly platinum electrocatalyst. Here, tandem PEC cell II generates 45 \( \mu A \) cm\(^{-2}\) (STH = 0.05%) without an applied bias and achieves an AB-STH efficiency of 0.59%, showing a much better stability than Cu\(_2\)O-BiVO\(_4\) (Table 3) without the need for nonconductive techniques and materials. To the best of our knowledge, PEC cell II’s AB-STH efficiency is the highest reported solar-to-hydrogen efficiency in a dual-photoelectrode tandem water splitting system that does not employ noble-metal cocatalysts (Table 3).\(^\text{[6,7,14]}\)

### 2.5. Medium-Scale Tandem PEC Cell

The success of PEC water splitting devices as a viable technology relies ultimately on the scalability of such systems.\(^\text{[27]}\) We have therefore investigated a medium-scale tandem system combining the better-performing nanoBiVO\(_4\)|TiCoOEC photocathode with a p-Si|TiNi|HEC photocathode in more detail. Since the measured photocurrent density of nanoBiVO\(_4\)|TiCoOEC was smaller than p-Si|TiNi|HEC on the small-scale, this electrode’s size was maximized to the greatest allowable illumination area (4 cm\(^2\)) in our PEC reactor.

Subsequently, p-Si|TiNi|HEC electrodes of different sizes were studied in order to match the overall photocurrent produced by this photocathode to that of the 4 cm\(^2\) photoanode. Ultimately, a 4-to-1 geometric surface area ratio between the BiVO\(_4\) and p-Si electrodes was employed in order to obtain a system with reasonably matched photocurrents over the practical applicable potential range (Figure 8a). In half-cell analysis, the p-Si|TiNi|HEC with a geometric surface area of 1 cm\(^2\) generated a photocurrent of \(-2\) mA at 0 V versus RHE, whereas nanoBiVO\(_4\)|TiCoOEC with a geometric surface area of 4 cm\(^2\) generated a photocurrent of \(-3.7\) mA at 0.6 V versus RHE. The comparatively reduced photocurrent densities in the larger electrodes are explained by increased IR drop in the system due to increased current loads, and by complications in maintaining uniform composite film loadings on the larger surfaces.

In this mid-scale PEC cell II, where the two photoelectrodes generate comparable photocurrents, the limitation of the two-electrode tandem cell performance is an operating compromise between the photoanode and the photocathode. This mid-scale tandem device achieved a maximum AB-STH of 0.28%, corresponding to a photocurrent of 1.96 mA at an applied bias of 0.6 V (Figure 8b). An additional 0.2 V of applied bias are required to produce this photocurrent when compared to the expected required bias derived from the photoelectrodes’ half-cell performance (Figure S17, Supporting Information); this additional device-based overpotential (more noticeable than on the smaller-scale) is attributed to the larger ohmic losses resulting from the increased current loads. Nonetheless, a PEC current of almost 2 mA at an applied bias of 0.6 V under standardized solar light irradiation is the highest reported photocurrent (and thus the highest rate of \(H_2\) generation) for a dual photoelectrode PEC water splitting system, to the best of our knowledge.\(^\text{[6,28]}\) While these experiments demonstrate the plausibility of moving toward larger-scale PEC water splitting devices with the current materials, they also serve to highlight some of the challenges that must still be overcome in scaling such systems.

### 3. Conclusions

In this work, the application of SSP chemistry for preparing multifunctional composite coatings for photoelectrodes has been reported, along with the use of these composite-coated photoelectrodes in PEC water splitting. Ti-/Ni- and Ti-/Co-containing films can be easily and inexpensively prepared by drop-casting or spin-coating SSPs onto a range of conductive and semiconducting substrates under ambient conditions. The TiNi and TiCo films act as precursors to bifunctional HECs and multifunctional composite coatings for photoelectrodes has been reported, along with the use of these composite-coated photoelectrodes in PEC water splitting. Ti-/Ni- and Ti-/Co-containing films can be easily and inexpensively prepared by drop-casting or spin-coating SSPs onto a range of conductive and semiconducting substrates under ambient conditions. The TiNi and TiCo films act as precursors to bifunctional HECs and OECs for water splitting in pH 9.2 electrolyte solution, demonstrating compatibility for applying these catalyst films onto water splitting photoelectrodes under the same conditions. In addition to serving as bifunctional electrocatalysts, TiNi and...
TiCo also act as SSPs to form an amorphous TiO$_2$ layer for protecting the semiconductor electrodes, thereby enhancing their photostability. We have therefore demonstrated for the first time that a multifunctional material can be integrated with photoelectrodes for application in solar water splitting, while using an approach that does not require prohibitively expensive or nonscalable materials, techniques, or experimental conditions.

Optimized photocathode and photoanode pairs were subsequently combined and tested in tandem PEC water splitting. Close-to-quantitative H$_2$ and O$_2$ gases were generated in a near two-to-one ratio with a benchmark AB-STH efficiency of 0.59% in a PEC cell with p-Si|$\text{TiNi HEC}$ wired to nanoBiVO$_4$|$\text{TiCo OEC}$ in a Bi$_2$SO$_4$ (pH 9.2) electrolyte solution (0.1 M Bi and 0.1 M K$_2$SO$_4$) with a scan rate of 5 mV s$^{-1}$. The complete composition of Cu$_2$O is FTO/Au/Cu$_2$O/Al/ZnO/TiO$_2$/RuO$_2$, where TiO$_2$ was prepared by ALD and RuO$_2$ acts as a HEC. H$_2$ and O$_2$ were not quantified and STH was calculated based on the photocurrent measured at 0 bias. Unbiased photocurrent only observed at >2 Sun illumination (200 mW cm$^{-2}$), data shown for 10 Sun. A fully integrated system of nanostructures with Pt as a HEC and IrO$_2$ as an OEC. Data shown for 1.5 Sun.

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4. Experimental Section

Preparation of TiN$_{SSP}$ and TiCo$_{SSP}$. TiNi$_{SSP}$ and TiCo$_{SSP}$ were synthesized and characterized as reported previously.$^{[1,2]}$

Preparation of Electrodes: FTO|$\text{TiNi pre}$ and FTO|$\text{TiCo pre}$ electrodes were prepared by drop-casting a TiNi$_{SSP}$ (2 × 20 µL, 5 × 10$^{-3}$ M in dry toluene) or TiCo$_{SSP}$ precursor solution (2 × 20 µL, 10 × 10$^{-3}$ M in dry toluene) onto an FTO-coated glass substrate (Pilkington; TEC Glass 7; sheet resistance 7 Ω sq$^{-1}$, 1 cm$^2$ exposed surface area). The as-prepared electrodes were then dried in air at room temperature prior to use. FTO|$\text{TiNiOEC}$ and FTO|$\text{TiCoOEC}$ electrodes were obtained by cycling the electrochemical potential five times between 0.6 and 1.9 V versus RHE with a scan rate of 50 mV s$^{-1}$. FTO|$\text{TiNiOEC}$ and FTO|$\text{TiCoOEC}$ electrodes were formed electrolytically in an aqueous Bi solution (0.1 M, pH 9.2) with K$_2$SO$_4$ (0.1 M) as supporting electrolyte using $E_{\text{app}} = -0.6$ V versus RHE for 10 min.

Figure 8. a) LSV scans of p-Si|$\text{TiNi HEC}$ (black, geometric surface area: 1 cm$^2$) and nanoBiVO$_4$|$\text{TiCo OEC}$ (red, area: 4 cm$^2$) measured in an aqueous pH 9.2 electrolyte solution (0.1 M Bi and 0.1 M K$_2$SO$_4$) with a scan rate of 5 mV s$^{-1}$. An Ag/AgCl/KCl sat$^{-}$ electrode was employed as the reference electrode, and a platinum foil as the counter electrode. The photocurrent of nanoBiVO$_4$|$\text{TiCo OEC}$ was measured under chopped solar light irradiation (100 mW cm$^{-2}$, AM 1.5G), whereas the photocurrent of p-Si|$\text{TiNi HEC}$ was measured in the tandem cell position (illumination filtered by nanoBiVO$_4$|$\text{TiCo OEC}$). b) LSV scan of tandem PEC cell II (two electrode configuration) consisting of a 1 cm$^2$ p-Si|$\text{TiNi HEC}$ and a 4 cm$^2$ nanoBiVO$_4$|$\text{TiCo OEC}$ under same conditions as (a).
The p-Si photocathodes were prepared from commercial boron-doped Si wafers (University Wafers; resistivity of 1–10 Ω cm; 100) single-side polished). The electric contact was formed using a GaIn eutectic solution (99.99%; Sigma-Aldrich) and a copper wire covered with a conductive silver epoxy resin (RS Components Ltd.). The geometric surface area of 0.5 cm² of the photocathodes was defined using Teflon tape for small-scale PEC measurements and was 1 cm² for mid-scale PEC measurements. Before the deposition of the SSPs, the silicon surface was cleaned with sequential treatments of H₂O₂ (30 wt% in H₂O; Fisher Scientific), H₂SO₄ (95%–98%; Sigma-Aldrich), and HF (65%; Merck Millipore) for 1 min at each step. p-Si/TiNiOEC and p-Si/TiCoOEC were prepared by drop-coating TiNiOEC (30 µL cm⁻², 2.5 × 10⁻³ m in dry toluene) and TiCoOEC (30 µL cm⁻², 5 × 10⁻¹ m in dry toluene) four times on the Si substrate, followed by cathodic in situ activation at E_{cell} = 0 V versus RHE under solar light irradiation in a B, solution (0.1 m, pH 9.2) with K₂SO₄ (0.1 M) as supporting electrolyte for 10 to 20 min.

NanoWO₃[6a,11c] and nanoBiVO₄[7a] were synthesized following published procedures. NanoWO₃/TiNiOEC and nanoWO₃/TiCoOEC were prepared by spin-coating TiNiOEC (60 µL cm⁻², 5 × 10⁻³ m in dry toluene) and TiCoOEC (60 µL cm⁻², 10 × 10⁻³ m in dry toluene) four times on the nanoWO₃ substrate, respectively. NanoBiVO₄/TiNiOEC and nanoBiVO₄/TiCoOEC were prepared by spin-coating TiNiOEC (20 µL cm⁻², 2.5 × 10⁻³ m in dry toluene) and TiCoOEC (20 µL cm⁻², 5 × 10⁻¹ m in dry toluene) four times on nanoBiVO₄, respectively. The geometric surface areas of the photoanodes were defined using a 1350 F polyester tape 3M (0.5 cm²) for PEC measurements and the precise geometric area was determined after the PEC measurements. Mid-scale (≈5 cm²) nanoBiVO₄/TiCoOEC electrodes were prepared by spin-coating TiCoOEC (5 × 10⁻¹ m) on nanoBiVO₄ for eight cycles.

Electrochemical and PEC Measurements: All electrochemical and PEC measurements were recorded with an iVum CompactStat potentiostat with a one-compartment electrochemical cell with two compartments separated by a Nafion 117 proton exchange membrane. For three-electrode experiments, an Ag/AgCl/KCl sat. electrode was employed as the reference electrode and the photocathode as the back electrode in the same light compartment. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments.

Survey spectra were collected with a pass energy of 200 eV and 30 eV (V vs Ag/AgCl/KCl sat) radiation (1486.6 eV, 400 µm spot size, 36 W). Partial pressure) at 1 s intervals were made throughout the experiment. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments.

For tandem PEC cell studies, a two-compartment cell separated by a Nafion 117 membrane was used with the photoanode as the front electrode and the photocathode as the back electrode in the same light path. A solar light simulator (Newport Oriel, Xenon 150 W) was used as the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments. The light intensity was calibrated to the light source in all experiments.

Physical Characterization: SEM was conducted to study the surface morphology of electrodes (Phillips XL30-FEG). p-XRD analyses were carried out using an X'Pert PRO X-ray diffractometer (Panalytical B.V.). Surface compositions of the electrode were verified by XPS (AXIS Ultra DLD Kratos Analytical, with the CasaXPS software) using a high power monochromatic Al Kα radiation (1486.6 eV, 400 µm spot size, 36 W). Survey spectra were collected with a pass energy of 200 eV and 30 eV sweeps, whereas high-resolution spectra were collected at a pass energy of 40 eV with ten sweeps.

Hydrogen and Oxygen Measurements: Oxygen was analyzed in the headspace of the anodic compartment of the PEC cell using an Ocean Optics fluorescence oxygen probe (FOXY-R). The probe was inserted through a tightly sealed septum and continuous O₂ readings (O₂ partial pressure) at 1 s intervals were made throughout the experiment. For electrocatalytic O₂ production with FTO|TiCoOEC, a potential of 2.0 V versus RHE was applied between 0.5 and 6.5 h of the experiment with the first 0.5 h as control with no applied potential. For PEC O₂ production by nanoBiVO₄|TiCoOEC in a three-electrode system, the cell was operated at an applied potential of 1.23 V versus RHE in the dark during the first 0.5 h (control experiment), followed by 1 h under standardized light illumination (100 mW cm⁻²) and another 0.5 h in the dark (control experiment). For O₂ quantification in PEC cell I, an applied bias of 0.8 V was applied in the dark during the first 0.5 h (control experiment), followed by 1 h under illumination and another 0.5 h in the dark (control experiment). In the case of tandem PEC cell II, the cell was operated at an applied bias of 0.6 V with the same dark-light-dark intervals. The control experiment is used for determining leakage of O₂ from the atmosphere into the cell and the resulting data were corrected for the derived rate of O₂ leakage. The total amount of O₂ evolved was determined as the sum of O₂ measured in the headspace using the ideal gas law plus dissolved O₂ in the solution calculated by Henry’s Law.

The amount of H₂ generated in the headspace of the cathodic compartment was detected and quantified with an Agilent 7890A Series gas chromatography equipped with a 5 Å molecular sieve column (Ν2 carrier gas at a flow rate of ≈3 mL min⁻¹). The gas chromatography oven kept the columns at 45 °C, and a thermal conductivity detector was used. The electrochemical cell was purged with 2% CH₄ in N₂ for at least 20 min prior to PEC experiments; methane served as an internal standard for H₂ quantification by gas chromatography. Using a syringe, the headspace gas was removed from the airtight electrochemical cell for gas chromatography analysis after electrochemical or PEC experiments.

The total amount of H₂ evolved was determined as the sum of H₂ measured in the headspace using the ideal gas law plus dissolved H₂ in the solution calculated by Henry’s law.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. Additional data related to this publication is available at the University of Cambridge data repository (https://www.repository.cam.ac.uk/handle/1810/252335).

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