Bulky crystalline BiVO$_4$ thin films for efficient solar water splitting

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We report a new fabrication method of flat, uniform BiVO$_4$ films on an electrically conductive transparent indium tin oxide (ITO) film based on a solution process for depositing bismuth precursor films and a high-temperature calcination process with an organic vanadium precursor. The synthesised BiVO$_4$ films, composed as a monolayer of crystallites (diameter ≤ 1 μm) fixed on the ITO, realised half-cell solar-to-hydrogen energy conversion efficiencies of over 1.5% by the aid of impregnated CoO$_x$ and atomic-layer-deposited NiO when tested as oxygen-evolving photoanodes for water splitting under solar simulator AM 1.5G illumination. Stoichiometric oxygen and hydrogen were generated with Faraday efficiencies of unity over 12 h at 0.6–0.9 V$_{RHE}$. This morphology of our bulky semi-transparent BiVO$_4$ films exhibited state-of-the-art solar water splitting performances.

Introduction

Photoelectrochemical (PEC) water splitting — harvesting solar energy to produce clean and renewable hydrogen fuels from water — is a promising technique to fulfill the increasing energy demands of modern society with minimum environmental impacts.$^{1-3}$ Considerable efforts have been made to realize high-performance and low-cost PEC overall water splitting devices. In PEC hydrogen evolution reactions (HERs), high solar energy conversion efficiencies are achieved when p-type semiconductors that are excellent light absorbers with high carrier mobility are used in photocathode-based half-cell PEC devices.$^{5,6}$ However, the development of efficient and stable photoanodes for oxygen evolution reactions (OERs) is still a challenging field.

One essential problem that impedes photoanode efficiency is the high activation energy associated with the complex four-electron OER process.$^2$ Holes easily recombine at photoanode/electrolyte interfaces before they oxidise water. Earth-abundant CoPi$^*$ and Ni/Fe layered-double-hydroxide (LDH)$^{7,8}$ have been developed as robust catalysts to largely improve OER kinetics in bias-driven PEC electrolysis. Besides the decoration of effective OER catalysts, suppression of charge recombination at photoanode surfaces by conformal coating of p-type materials has been reported.$^{9,10}$ In this way, dangling bonds at photoanode surfaces are passivated and buried p/n junctions are created to increase the hole lifetime.

Suppression of charge recombination in the photoanode bulk is another fundamental aspect for improving PEC performances. Photoanode materials that can effectively separate charges and efficiently transport holes are required. BiVO$_4$ is one of the most attractive candidates,$^{10-12}$ due to its deep valence band for OER under visible light and long-term stability in near-neutral aqueous solutions. Further, BiVO$_4$ has a long carrier lifetime of ~40 ns compared to that of <10 ps for other oxide photocatalysts such as hematite.$^{13,14}$ However, the carrier mobility in BiVO$_4$ is low at ~0.044 cm$^2$ V$^{-1}$ s$^{-1}$, indicating that most of the photo-generated holes are localised in BiVO$_4$.

To achieve efficient charge separation in BiVO$_4$, attempts have been made on fabricating (1) monolayer BiVO$_4$ sub-micro nanoparticles on conducting Ti metal by particle transfer methods,$^8$ (2) BiVO$_4$ homo-/hetero-junctions such as BiVO$_4$/WO$_3$/ITO films$^{10,14}$ and (3) nanostructures such as nanowire arrays.$^{15,16}$ Recently, Choi et al. reported nanoporous BiVO$_4$ with state-of-the-art photocurrent density and efficiency.$^{12}$ A simple and effective electrodeposition–annealing process was applied for synthesising nanoporous BiVO$_4$ with particle sizes of ~80 nm. Nanostructures drastically improve charge separation and surface areas for largely enhanced PEC performances.

However, nanostructures have disadvantages that warrant special care with respect to their practical applications. (1) Their mechanical strength is not satisfactory and achieving mechanical robustness is a stubborn challenge for practical operation. It is difficult to improve the mechanical strength of certain materials, especially nanostructured materials. (2) Coating of other functional materials over entire nanostructures is also difficult compared to that for flat thin films. This further hampers the construction of tandem devices when starting with nanostructures.

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In contrast, multi-layered tandem film devices with anti-reflective coatings are commercialised for solar cells. Thus also for PEC applications aiming for future industrialisation, it is desirable to fabricate robust and flat BiVO₄ thin films with exact stoichiometry, the most photoactive crystallographic structure, and high crystallinity with the particle size optimised.

In this study, we present an anodic electrodeposition and calcination process for fabricating bulky BiVO₄ crystalline films on transparent ITO glass for use as photoanodes in solar water splitting cells. The fabricated films were proven to be mechanically robust. After surface decoration with CoOₓ catalysts and conformal deposition of NiO layers, a half-cell solar-to-hydrogen (HC-STH) conversion efficiency of over 1.5% was realised. Stoichiometric hydrogen and oxygen were generated with unity Faraday efficiency over 12 h.

**Experimental**

**Deposition of Bi precursor thin films**

First, 25 mL 0.1 M Bi(NO₃)₃ in acetic acid was prepared. The pH of the prepared solution was adjusted to 4.8 by adding 5 M NaOH aqueous solution. Then 20 mL 0.3 M p-benzoquinone in ethanol (99.95%) was added into the solution. After gently stirring for 1 h, the colour of the solution changed to transparent dark brown. Electrodeposition in this mixture was performed on ITO glass plates (Geomatec, sheet resistivity ~ 5 Ω sq⁻¹, 30 mm × 10–30 mm × 1 mm thickness). A potentiostat (Hokuto Denko, HSV-100) was used at room temperature with ITO glass as the working electrode, an Ag/AgCl reference electrode and a Pt counter electrode. The ITO working electrode was maintained at 2.3 VAg/AgCl. The optimised deposition time was 7 min.

**Synthesis of BiVO₄ thin films**

The Bi precursor film was drop-painted with a 1 : 1 dimethyl sulfoxide/ethanol solution of vanadyl diacetylacetonate (VO(acac)₂, 0.2 M). The casting amount was 0.075 mL for a 20 mm × 20 mm Bi precursor film. The VO(acac)₂/Bi precursor film was calcined at 500 °C in air (heating rate of 2 °C min⁻¹ and then cooled down naturally). (C) BiVO₄ films prepared by calcining as-deposited BiCₓOᵧ with 0.5 mM VO(acac)₂/1 : 1 ethanol + DMSO for 1 hour in air. The substrate pieces of glass were all 20 mm × 30 mm in size.

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**Fig. 1** Sample Bi precursor films and BiVO₄ films on ITO glass. (A) Bi precursor film after the deposition of BiCₓOᵧ. The initial BiCₓOᵧ was deposited in 25 mL 0.1 M Bi(NO₃)₃/CH₃COOH + 20 mL 0.3 M p-benzoquinone/C₂H₅OH (pH adjusted at 5.3) at 2.3 VAg/AgCl for 7 min. (B) BiCₓOᵧ heated at 500 °C in air (temperature ramped up to 500 °C with a heating rate of 2 °C min⁻¹ and then cooled down naturally). (C) BiVO₄ films prepared by calcining as-deposited BiCₓOᵧ with 0.5 mM VO(acac)₂/1 : 1 ethanol + DMSO for 1 hour in air. The substrate pieces of glass were all 20 mm × 30 mm in size.

**Fig. 2** X-ray diffraction spectra of (A) a bare ITO glass piece (Geomatec, ITO thickness ~ 500 nm, sheet resistivity ~ 5 Ω sq⁻¹), (B) the as-deposited BiCₓOᵧ, (C) BiCₓOᵧ heated at 180 °C in air, (D) at 300 °C, (E) at 500 °C, (F) BiVO₄ film by calcination of as-deposited BiCₓOᵧ, and VO(acac)₂ at 520 °C for 1 h, (G) an expanded spectrum from curve (F) for (024) and (204) diffractions of the scheelite monoclinic BiVO₄. The X-ray wavelength was 0.15418 nm (Cu Ka). The standard diffraction peak positions are indicated by + at the top, referring to ref. 25 for BiO, ref. 26 for Bi₂O₃ and ref. 27 for BiVO₄.
Fig. 3  SEM images of precursors and completed BiVO₄ films. (A) Top view of as-deposited BiCₓOᵧ. (B) The cross section of as-deposited BiCₓOᵧ.
On the right of this image, (a) BiCₓOᵧ, (b) a gap accidentally made when clamping this sample, (c) ITO, (d) glass. (C) Top view of BiCₓOᵧ heated at 500 °C. (D) Top view of the BiVO₄ film by calcination of as-deposited BiCₓOᵧ, and VO(acac)₂ at 520 °C for 1 hour. Rinsed in 1 M NaOH. (E) A magnification of the central part of (D). (F) Top view of the BiVO₄ film by calcination of BiCₓOᵧ, pre-heated at 500 °C (equivalent to image C) and then with VO(acac)₂ at 520 °C for 1 h. Rinsed in 1 M NaOH. (G and H) Cross sections of the final BiVO₄ film (equivalent to image D), (e) BiVO₄, (f) ITO, (g) glass. (I) Top view of a BiVO₄ film modified by impregnation of CoOₓ and ALD of NiO. (J) NiO/CoOₓ/BiVO₄ photoelectrode after PEC performance test at 0.6 V_RHE for 48 hours.
calcined in a muffle furnace in air at various temperatures from 490–530 °C. The excess amount of VO₂ was washed away in 1 M NaOH solution for 10 min with gentle stirring. The obtained BiVO₄ films were then cleaned with DI water and dried at room temperature. In our experiments, BiVO₄ films synthesised at 520 °C for 2 h with the initial temperature ramping rate of 2 °C min⁻¹ exhibited the best performance.

**Loading of CoOₓ on BiVO₄**

The BiVO₄ films were immersed in a 20 mL 0.01 M Co(NO₃)₂ and 0.01 M NH₃ H₂O solution at pH 8.4 for 0.5 h. Then the films were washed with DI water and annealed in air at 250 °C for 0.5 h.

**Atomic-layer deposition of NiO on CoOₓ/BiVO₄**

Atomic-layer deposition (ALD) was applied to deposit NiO on the CoOₓ/BiVO₄ films. Bis-[2,2,6,6-tetramethylheptane-3,5-dionato] nickel(n) [Ni(thd)₂] in short) and H₂O were used as the precursors. Ni(thd)₂ was heated to 165 °C and H₂O was set to 15 °C. The temperature in the deposition chamber was 260 °C. One ALD cycle consists of an H₂O pulse for 6 s, N₂ purging for 3 s, pressurising the Ni(thd)₂ container by N₂ gas (500 sccm) for 3 s, a Ni(thd)₂/N₂ pulse for 6 s, and a N₂ purging for 3 s. Before ALD, CoOₓ/BiVO₄ was treated in an ozone plasma cleaning machine for 5 min to increase surface wettability with respect to hydroxyl ions. For BiVO₄ films, 300 cycles ALD delivered the best performances. Excess deposition of NiO on CoOₓ/BiVO₄ could be thinned by 50 mV s⁻¹ cyclic-voltammetry scans from −0.6 to 0.8 VAg/AgCl in a 1 M pH 6 Na₂SO₄ solution.

**Characterizations**

Scanning electron microscopic (SEM) observations were carried out using a Hitachi SU8020 system. The X-ray diffraction (XRD) was measured by a SmartLab XRD (Rigaku, Japan). The X-ray wavelength was 0.15418 nm (Cu Kα).

The PEC performances were investigated using a three-electrode electrochemical configuration in a 0.5 M potassium borate (K₂B₄O₇) buffer solution at pH = 9.5 by a solar simulator light source (SAN-EI electronic, XES40S1). The light intensity of this solar simulator was adjusted to AM 1.5G (100 mW cm⁻²) by measuring with a calibrated photometer (Hamamatsu model S2281). The electrolyte was stirred and bubbled with Ar gas before and during measurements. An Ag/AgCl electrode in saturated KCl solution was used as a reference electrode and a Pt coil was used as the counter electrode. The potential unit is converted to the reversible hydrogen electrode according to the Nernst equation,

\[
V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.059 \text{pH} + \frac{1}{2} V_{\text{Ag/AgCl}}
\]

\[
V_{\text{Ag/AgCl}} = 0.199 \text{V at 25 °C}
\]

The incident light spectral analysis for the photocurrent was performed using a Xe lamp (Asahi Spectra, MAX-302) equipped with bandpass filters (central wavelengths: 400–540 nm, every 20 nm; full width at half maximum: 10 nm). The irradiance spectra of the light incident on the electrode surface were measured with a spectroradiometer (EKO Instruments, LS-100, absolutely calibrated for the intensity).

The gas chromatographic (GC) quantification of H₂ and O₂ during the PEC H₂O splitting was performed with a dedicated setup. An air-tight three-electrode PEC cell with NiO/CoOₓ/BiVO₄ working electrodes, Ag/AgCl reference electrodes and Cr-coated Pt counter electrodes was used for GC analyses. Here, Cr was coated on Pt wire to suppress the reverse reaction of oxygen reduction on the Pt wire in solution. The PEC cell was connected to a vacuum pump and a micro GC (Inficon Co., Ltd, 3000). Before measurement, the PEC cell was pumped to a low vacuum and then purged with Ar sufficiently to get rid of N₂ and O₂ gases in the PEC cell. H₂ and O₂ evolution were measured in 0.5 M K₂BO₃ buffer solution at pH 9.5 under simulated sunlight illumination for 12 h with potential vs. RHE at 0.6 and 0.9 V_RHE.

The electric current passing through the outer circuit was obtained by measuring the same amounts of H₂ and O₂ gases in the PEC cell. One ALD cycle consists of an H₂O pulse for 6 s, N₂ purging for 3 s, pressurising the Ni(thd)₂ container by N₂ gas (500 sccm) for 3 s, a Ni(thd)₂/N₂ pulse for 6 s, and a N₂ purging for 3 s. Before ALD, CoOₓ/BiVO₄ was treated in an ozone plasma cleaning machine for 5 min to increase surface wettability with respect to hydroxyl ions. For BiVO₄ films, 300 cycles ALD delivered the best performances. Excess deposition of NiO on CoOₓ/BiVO₄ could be thinned by 50 mV s⁻¹ cyclic-voltammetry scans from −0.6 to 0.8 VAg/AgCl in a 1 M pH 6 Na₂SO₄ solution.

**Results and discussion**

Fig. 1 shows photographs of ITO glass plates covered by an as-deposited Bi precursor film, a Bi precursor film annealed at 500 °C, and the BiVO₄ film prepared according to the above-mentioned procedures. We temporarily call the precursor film BiCₓOᵧ. The as-deposited BiCₓOᵧ film might be hydrated and contain carbonate and other carbonaceous components. Bubbles were seen when this film was immersed in dilute HCl, and the gas was probably CO₂. During the electrochemical deposition process, CH₃COO⁻ in pH 5–6 solution can be altered into CO₃²⁻ by Kolbe electrolysis. The mechanism of Bi accumulation on this positively polarised electrode must include elementary reactions involving CH₃COO⁻, which is the major component of this solution.

Annealing the BiCₓOᵧ film in a muffle furnace in air altered the colour of the film. Before annealing, the as-deposited BiCₓOᵧ film looks brown (Fig. 1A), and after annealing at 500 °C the colour is close to white (Fig. 1B). The change in colour is related to the changes in the Bi compounds in the film. XRD spectra were recorded for the films from as-deposited BiCₓOᵧ and annealed BiCₓOᵧ, shown in Fig. 2B–E. The spectra always contain diffractions from the substrate ITO (A). The as-deposited BiCₓOᵧ and annealed samples below 300 °C exhibit broad scattering at 28° of the diffraction angle (Fig. 2B). The films were amorphous, probably composed of nano-crystallites of Bi carbonaceous compounds. The components of BiCₓOᵧ might be those such as bismuth carbonate, bismuth hydroxide carbonate, and other carbonaceous materials. Above the annealing temperature of 300 °C, XRD exhibited sharp peaks (Fig. 2D and E), better matching the standard peak positions of crystalline BiO than those of Bi₂O₃ (Fig. 2 top). We carried out
The photoelectrochemical (PEC) performance tests for the bare BiVO₄ and NiO/CoOₓ/BiVO₄ photoelectrodes by AM 1.5G solar simulator excitation in a 0.5 M K₃BO₃ solution adjusted to pH 9.5. (A) The photocurrent density (j/mA cm⁻²) as a function of the electrode potential (E/V_RHE). Blue curve: by PEC measurement with chopped light for a bare BiVO₄ electrode. Red curve: our best-performance NiO/CoOₓ/BiVO₄ electrode with an active surface area of 0.95 cm². Black bold line: average curve for 10 new different NiO/CoOₓ/BiVO₄ electrodes. Broken black line: average dark currents for the same samples. (B) the half-cell solar-to-hydrogen (HC-STH) conversion efficiency. (C) Time course of H₂ and O₂ evolution with at E = 0.6 V_RHE and E = 0.9 V_RHE for 12 h. The colour codes are: red = H₂, 0.6 V_RHE, blue = O₂, 0.6 V_RHE, purple = H₂, 0.9 V_RHE, green = O₂, 0.9 V_RHE.

Fig. 4 The wavelength dependence of incident photon conversion efficiency (IPCE) of a NiO/CoOₓ/BiVO₄ photoelectrode of the average performance in a 0.5 M K₃BO₃ solution at pH 9.5. The photocurrent was recorded within 10 min after starting chronoamperometric measurement, using the bandpass-filtered Xe lamp. The IPCE values are calculated by IPCE = j(λ)/P(λ)/(hc/λ), where λ: monochromatic light wavelength/nm, j(λ): current density/mA cm⁻², P(λ): light power density/mW cm⁻², e: electron charge = 1.60 × 10⁻¹⁹ C, h: Plank constant = 6.63 × 10⁻³⁴ J s, and c: light speed = 3.00 × 10⁸ m s⁻¹.

The annealed film is compositionally close to BiO (Bi 92.9% w/w) or Bi₂O₃ (Bi 89.7% w/w). Although there were some residual carbonaceous materials therein, the films annealed at 500 °C were determined to be mainly composed of crystalline BiO.

The morphological change of BiC₀ₓ upon annealing is visualised by scanning electron microscopy, as shown in Fig. 3. The original as-deposited BiC₀ₓ comprised a flat, smooth, homogeneous layer with a thickness of ~300 nm (Fig. 3A and B). The top view indicates that the film consists of fine grains (diameter < 10 nm). As annealing temperature was raised and reached 500 °C, the grain size increased up to 1 μm (Fig. 3C). The grains compose a monolayer over the ITO surface and some voids are seen surrounded by grains. This bulky morphology of BiO particles is the prototype of BiVO₄ films, as discussed later.

Calcination of the as-deposited BiC₀ₓ with vanadyl bis-acetylacetonate (VO(acac)₂) at 520 °C formed highly crystalline BiVO₄ of scheelite monoclinic type, as seen in the XRD spectra in Fig. 2F and G. Splitting of the BiVO₄ (024) and (204) peaks at 46.7° and 47.3° (Fig. 2B) was clearly observed. This is essentially different from the single (024) peak of ~47° for tetragonal BiVO₄. Note that there is no ITO peak between 46° and 48°, which rules out the other possibility for this XRD peak splitting.

Elemental analysis of the as-deposited BiC₀ₓ film and BiC₀ₓ film annealed at 500 °C, having scratched them off from the ITO glass. This powder was subjected to decomposition in HNO₃ and Bi quantification by means of inductively coupled plasma (ICP) spectroscopy. The Bi contents for as-deposited BiC₀ₓ film and BiC₀ₓ film annealed at 500 °C were 76.8% w/w and 86.4% w/w, respectively.

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The BiVO₄ films calcined at different temperatures between 490 °C and 530 °C were all of the same monoclinic structure. The synthesised BiVO₄ is made of large BiVO₄ particles with an in-plane diameter of ~1 μm and a thickness of ~300 nm (Fig. 3D and E). Some grains, probably depending upon the crystallographic orientation, have a bunch of needle-like shapes aligned along one direction.

It is notable that the final BiVO₄ particles (Fig. 3D and E) look quite similar in size and in shape to the BiO particles formed by annealing at 500 °C (Fig. 3C). Actually BiC₂O₄ pre-annealed at 500 °C was subjected to calcination with VO(acac)₂ at 520 °C. The same shape of BiVO₄ crystallites (Fig. 3F) appeared as seen in Fig. 3D and E. Presumably the temperature ramping of BiC₂O₄ + VO(acac)₂ from room temperature induces the formation of BiO crystallites near 500 °C, and the BiO crystallites are converted into BiVO₄ crystallites simultaneously with diffusion of V.¹⁷–²⁰

The BiVO₄ crystallites formed a particle monolayer firmly fixed on ITO. The in-plane diameter of BiVO₄ crystallites is larger than that of the previously reported BiVO₄ nanostructures or films synthesised by spray pyrolysis,¹¹ electrochemical processes,²² chemical vapour deposition²² or co-evaporation.²¹

The two-step synthesis of BiVO₄ was first reported by Choi and co-workers using BiO iodide as a starting material.²² The key step in their synthesis is the fabrication of very thin BiOI nanosheets that have a large surface area to make the Bi and V precursors be sufficiently in contact with each other for uniform BiVO₄ nucleation during calcination. Differently from their BiO iodide cathodic deposition, we fabricated a dense Bi precursor film on ITO as anodes. The Bi precursor film is advantageous for the fabrication of bulky crystalline BiVO₄ films, evidenced by the conversion from BiO crystallites observed by XRD and SEM analyses as described above.

The present BiVO₄ films were mechanically robust. The film never came off even when subjected to pressing, rubbing or scratching by a finger or wiping with tissue paper. More systematically, we performed a peeling-off test with adhesive tape. A piece of adhesive tape (“mending tape”) was applied on the films, and pressed by loading a weight over the tape at 220 g cm⁻² for 1 min. Then the tape was peeled off and the glue surface of the tape was inspected. In the case of present BiVO₄ films, nothing looked transferred to the adhesive. The nanoporous films we reproduced according to the recipe²³ did not survive these tests and released BiVO₄ dust. This demonstrates the high reliability of this BiVO₄ crystalline monolayer towards usage under mechanically severe conditions, such as in a flow of electrolytic solutions or in repetitive heating/cooling cycles.

As for the O₂-evolution cocatalysts, CoO₂ was loaded on BiVO₄ films by impregnation, and atomic layer deposition (ALD) was performed to deposit NiO on the surface of CoO₂-loaded BiVO₄. After PEC measurement, NiOOH was formed on the top surfaces of NiO nanoparticles (Fig. 3J). This state of the NiOOH are supposed to contain a large amount of surface hydroxyl ions for efficient OERs.²⁷ Ultrathin NiOOH can allow penetration of hydroxyl ions and also enable hydroxyl ions to be in contact with the buried CoO₉ for a dual OER catalyst effect.²⁷,²¹ A small amount of Co incorporation in NiOOH can also possibly increase its electric conductivity to reduce applied potential loss within the NiOOH layer, for realising high PEC performances.⁷,¹²,²⁴

The PEC performance of the bare BiVO₄ and NiO/CoO₂/BiVO₄ photoanodes was measured in 0.5 M pH 9.5 potassium borate (K₂B₄O₇) buffer solutions under simulated air mass (AM) 1.5g illumination. Fig. 4A shows the photocurrent density (j) as a function of the electrode potential (E). The chopped light blue and red j–E curves represent the PEC performances of our bare BiVO₄ electrode and our best NiO/CoO₂/BiVO₄ electrode, respectively. The best electrode had a light acceptance/electrolytically active area of 0.95 cm². The black j–E curve is an average PEC performance from j–E curves obtained with 10 different NiO/CoO₂/BiVO₄ test samples, with the average dark current also shown. We take this average data as the representative characteristics of the present NiO/CoO₂/BiVO₄ photoanode. The photocurrent onset potential was ~0.2 V_RHE in Fig. 4A. The anodic photocurrent at this low applied-bias region indicates the effective separation of photogenerated charges and efficient migration of holes towards BiVO₄ surfaces for OERs. The photocurrent density is over 2.5 mA cm⁻² at 0.6 V_RHE for the NiO/CoO₂/BiVO₄ photoanode. The HC-STH curves, shown in Fig. 4B, are calculated from the j–E curves by

\[ \text{HC-STH} = (1.23E/V_{\text{RHE}})/(\text{solar simulator power/W cm}^{-2}) \]

The average HC-STH curve reaches the maximum of 1.5% at 0.56 V_RHE, which was markedly high among the reported single-photon photoanodes. High performance of the semi-transparent BiVO₄ films is suitable for the construction of parallel electrode devices, such as integrated solar water splitting devices with a narrow-bandgap photocathode or photovoltaic cells placed behind BiVO₄/ITO/glass to utilize the transmitted solar photons through this semi-transparent electrode.

To confirm HERs at the Pt electrode and OERs at the NiO/CoO₂/BiVO₄ photoanode, the evolved gas was analysed by gas chromatography. The plots in Fig. 4C indicate the amounts of accumulated H₂ and O₂ gases within the PEC reactor measured by gas chromatography. The curves are obtained by integrating the photocurrent density as a function of time and converted into the accumulated amounts of H₂ and O₂ under the assumption that the photocurrent was completely consumed at the Pt cathode with 2 electrons for one H₂ molecule and at the BiVO₄ photoanode with 4 electrons for one O₂ molecule. The NiO/CoO₂/BiVO₄ photoanodes were held at constant potentials of 0.6 and 0.9 V_RHE in three-electrode configurations for 12 h. The evolution of H₂ and O₂ with a ratio of 2 : 1 was continuously demonstrated. The Faraday efficiency of HERs and OERs were both close to 100%, demonstrating that the photocurrent is all attributed to OERs and HERs.

The efficiency of the NiO/CoO₂/BiVO₄ photoanode was verified by measuring the wavelength dependence of incident photon conversion efficiency (IPCE), using the intensity-calibrated Xe lamp with bandpass filters. Fig. 5 shows the result. IPCE reaches 0.45 at 0.6 V_RHE and 420 nm, which matches the PEC photocurrent density at 0.56 V_RHE by supposing a constant IPCE below 420 nm and multiplying the whole absorbed solar spectrum.
The present bulky crystallite BiVO₄ thin film, with a superior mechanical robustness, exhibited high PEC performance and durability comparable to foregoing nanoporous and other types of O₂-evolving undoped BiVO₄ photoelectrodes.²⁻²²,²³ The robustness originates from the large BiVO₄ grain size, which is inherited from the precursor BiO film, derived from the BiC₂O₄ film deposited on ITO. The solid BiO calculation at 520 °C with diffusion of V from VO(acac)₂ is the key process for the uniform formation of stoichiometric scheelite monoclinic BiVO₄ without unbalanced agglomeration of the components. The purity and crystallinity of the light absorbing BiVO₄ grains are probably the reasons for the good charge carrying and separating properties. Although the specific surface area might be smaller than that of porous-type materials, the impregnated CoOₓ and ALD NiO formed conformal rough surfaces, acting as a highly active cocatalyst for O₂ evolution. The advantages of impregnated CoOₓ and ALD NiO cocatalysts were explained in detail in our previous report.⁸

Conclusions

We developed a new route for the synthesis of highly active, durable oxygen evolving, bulky crystalline BiVO₄ film photoanodes on ITO glass. After modification with impregnated CoOₓ and ALD NiO, the BiVO₄ electrode performs with a half-cell solar-to-hydrogen energy conversion efficiency of over 1.5% as an oxygen-evolving photoanode for water splitting under solar simulator AM 1.5G illumination. The high activity is maintained for 12 h at the operation potential of 0.6 and 0.9 V_RHE with continuous and stoichiometric hydrogen and oxygen evolution. Mechanical strength is one of the superior properties owing to the firmly fixed BiVO₄ crystallites on ITO substrates. The transparent characteristic of this electrode with respect to longer wavelength light in the solar spectrum further enables its use in tandem-type stand-alone water splitting devices assembled with hydrogen-evolving photocathodes made of narrow-bandgap p-type semiconductors.

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