Accepted Article

Title: Photoelectrochemical Performance of BiVO4 Photoanodes Integrated with [NiFe]-Layered Double Hydroxide Nanocatalysts

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Eur. J. Inorg. Chem. 10.1002/ejic.201701231

Link to VoR: http://dx.doi.org/10.1002/ejic.201701231
Abstract: We immobilized laser-made nickel iron layered double hydroxide ([NiFe]-LDH) nanocatalysts on BiVO₄ photoanodes. We compared photoelectrochemical performance of integrated [NiFe]-LDH–BiVO₄ photoanodes in sulfite-free aqueous electrolyte with photocurrent generation of neat BiVO₄ photoanodes in aqueous electrolyte with sulfite added as sacrificial hole acceptor. We optimized catalyst mass loading, which is a tradeoff between most efficient depletion of photogenerated holes that drive catalytic turnover and parasitic light absorption by the catalyst particles. We also mitigated nanocatalyst aggregation on the BiVO₄ surface by a surfactant that selectively ligated the catalysts or by dispersing the catalyst suspension more rapidly on the photoanode surface. Our rational optimization strategies enhanced photoelectrochemical performance of integrated nanocatalyst photoanodes: Two thirds of all photogenerated holes escaped loss processes in our optimized integrated [NiFe]-LDH–BiVO₄ photoanodes under 100 mW cm⁻² of simulated air mass 1.5G illumination in aqueous pH 9.2 buffered electrolyte. Our systematic optimization strategies for integration of highly efficient water oxidation nanocatalysts with a visible-light absorber provide a path towards functional artificial photosynthesis devices.

Introduction

Conversion of solar energy into high-energy-density fuels, such as hydrogen from water splitting or reduced forms of carbon dioxide from artificial photosynthesis, encompasses three processes: light capture, charge transport, and catalysis. All three must be optimized for maximum efficiency. Separation of light capture and catalysis mimics nature and is a particularly promising approach. We used here BiVO₄ photoanodes that we integrated with laser-made nanocatalysts, because we discovered in earlier work that they compared favorably with similar catalysts that were prepared by other methods.¹

Solar water oxidation is key to artificial photosynthesis (Scheme 1). Water oxidation must be the source of the protons and electrons needed for the upgrading of our most abundant feedstocks. In the future, reductive transformations of water, carbon dioxide, and nitrogen will produce our clean fuels, value-added commodity chemicals, pharmaceuticals, and fertilizers.

Scheme 1. Importance of solar water oxidation.

Great strides have been made in the development of photovoltaic components and catalysts.²⁻⁴ Semiconducting photoanodes for use in photoelectrochemical (PEC) tandem devices must be stable over long periods of time under turnover conditions, have band positions that are suitable for the charge oxidation reaction, and a bandgap that enables efficient absorption of sunlight. Although no existing material fits the bill for use in a practical device, we chose scheelite-type n-BiVO₄ for light capture because it absorbs visible light,⁵ is well investigated,⁶ and is stable over a wide pH range.⁷

Photocurrent generation of neat BiVO₄ is limited by its poor water oxidation activity and concomitant slow kinetics for oxygen evolution,⁸ which can be overcome by attachment of a water oxidation catalyst or addition of a sacrificial hole acceptor, such as sulfite, to the electrolyte. Sulfite has been shown to be a very efficient hole acceptor in aqueous photocatalysis and has been used extensively to study photocurrent generation in n-BiVO₄.⁹

If the sulfite concentration at the electrode surface is sufficiently high, sulfite is expected to react with all photogenerated holes at the electrode surface. Assessment of photoanode PEC performance in sulfite-containing electrolytes will, therefore, provide the true photo-hole production ability of BiVO₄.

Neat BiVO₄ photoanodes (i.e. electrode surface in direct contact with electrolytes) have been extensively investigated to assess the intrinsic PEC performance of n-BiVO₄ (see refs. ⁸, ¹₀ and references therein). Thus, the electronic properties of this semiconductor-liquid junction were optimized. Once a catalyst layer (which may be impermeable by the electrolyte) is deposited onto the BiVO₄ surface, however, the junction to the semiconductor is buried, fundamentally changing the junction electronics, such as band bending.¹¹ In other words, BiVO₄ photoanodes that were optimized in direct contact with the electrolyte will behave very differently when a catalyst layer is shielding them from the electrolyte.

Bismuth vanadate photoanodes with micrometre-diameter [NiFe]-LDH material have recently been reported.¹² The [NiFe]-

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LDH layer had a thickness of 1.5 µm, making it impractical for use in a real water-splitting device that must operate under front-side illumination. Here, we report strategies of integrating [NiFe]-LDH nanosheets with BiVO$_4$ photoanodes for use with front-side illumination. Our data on systematic optimizations reveal the processes that impede photocurrent generation. We used nanoparticulate catalysts that we deposited as discrete particles or aggregates. Nanocatalysts have the advantage that they avoid the formation of a buried junction because they are deposited such that some BiVO$_4$ is still exposed to the liquid electrolyte; at the same time, the catalysts may utilize the photogenerated holes to speed up the water-oxidation reaction. Hence, we expect that nanoparticles on BiVO$_4$ alter the light absorber’s electronic properties in the least possible way.

Integration of catalysts with photoelectrodes requires that (i) both materials are robust in the same electrolyte under PEC conditions, (ii) catalysts do not block sunlight from reaching the light absorber, (iii) attachment of catalysts onto photoanode surfaces does not diminish catalytic efficiency, and (iv) catalysts do not interfere with the photoanode’s electronic properties. Heterogeneities at the interface complicate photocatalysis as well.$^{[10]}$

Catalysts layers (prepared by (photo)electrodeposition, atomic layer deposition, or impregnation with cobalt(II) nitrate and calcination) or immobilized molecular catalysts on BiVO$_4$ surfaces have been reported.$^{[7b-e, 11]}$ Our method of drop casting nanocatalysts from aqueous suspensions is expected to alter the BiVO$_4$ surface less than electrodeposition, as under polarization ion diffusion (from the plating bath) into BiVO$_4$ or etching of the photoanode material may occur. Hole depletion may also be more efficient with nanoparticulate catalysts compared to layers.

We used nickel iron layered double hydroxide ([NiFe]-LDH) nanosheets (~12 nm diameter) as water-oxidation catalysts. We have shown in earlier work that these [NiFe]-LDH nanocatalysts are highly active and evolve oxygen with 100 % faradaic efficiency.$^{[12]}$ We synthesized them by pulsed-laser ablation in liquids without any capping agents or surfactants that would limit surface atom sites and block catalytic sites. In [NiFe]-LDH nanosheets, these catalytically active sites are iron centers located at the perimeter of the sheets, as we have recently shown.$^{[13]}$ Catalysis at these iron sites requires that they are accessible for the reactants. Importantly, our nanocatalysts can be readily drop cast from suspension onto any photoanode material, irrespective of its chemical stability under electrodeposition conditions.

We applied different strategies to overcome challenges of (hydr)oxide nanocatalyst deposition on metal oxide surfaces (Figure 1). Importantly, we aimed to maximize the number of accessible catalytic sites and minimize parasitic light absorption, reflection, or scattering. Dau et al. recently showed that NiFe oxyhydroxide catalysts that were dispersed on carbon supports exhibited enhanced activity because a larger population of metal centers was electrochemically addressable and accessible.$^{[14]}$ Surfactant-free nanoparticles aggregate.$^{[15]}$ Aggregation of metal oxide of hydroxide nanoparticles may be exacerbated upon deposition onto (chemically similar) metal oxide photoanode surfaces. Aggregates limit PEC performance because photogenerated holes must travel from BiVO$_4$ through multiple catalyst nanoparticles before reaching the electrolyte. The probability for adverse charge recombination rises as hole-transport distances become larger. Hence, nanocatalyst aggregation on photoelectrode surfaces causes charge carriers to be lost in competing processes.

Surfactants that bind to catalyst surfaces and keep individual particles separated mitigate nanoparticle aggregation but have detrimental effects on water-oxidation activity as catalytically active surface sites are blocked. As a result, the tradeoff between minimization of nanoparticle aggregation and blocking of catalytic sites by surfactant molecules must be optimized. We tested three surfactants with different chelating properties to reduce aggregation. We investigated surfactant and dispersant effects on the distributions of Co$_3$O$_4$$^{[16]}$ and [NiFe]-LDH nanocatalysts on BiVO$_4$ surfaces to show that our method to minimize aggregation is broadly applicable to nanocatalysts; additionally, we established the correlation between nanocatalyst distribution and photocurrent enhancement for Co$_3$O$_4$ on BiVO$_4$.

We also devised an alternative approach to spread nanocatalysts more evenly on metal oxide photoanode surfaces: dispersion of the aqueous nanocatalyst suspension droplet by a small amount of isopropanol during drop-cast deposition. Addition of isopropanol to water significantly improves the wetting on the BiVO$_4$ surface.

Besides catalyst particle distribution, absolute catalyst mass loading matters for optimized PEC performance, as the overall efficiency is a tradeoff between higher numbers of accessible, catalytically active surface sites and detrimental light absorption by the catalyst.

We prepared BiVO$_4$ photoanodes by spin coating on fluorine-doped tin oxide (FTO) coated glass slides and drop cast aqueous suspensions of [NiFe]-LDH nanoparticles onto these BiVO$_4$ photoanodes. We assessed morphologies and distributions of surface species by scanning electron microscopy (SEM) coupled with energy-dispersive spectroscopy (EDS) mapping. We measured photocurrent generation with front-side illumination because for practical use in an artificial photosynthesis device only front-side illumination will matter. In this work, we explored optimization strategies for integrated [NiFe]-LDH–BiVO$_4$ photoanodes.
Results and Discussion

We prepared neat BiVO₄ films on FTO-glass substrates by spin coating, using a procedure similar to a published report. XRD data of the yellow films were consistent with monoclinic scheelite-type BiVO₄ (Figure 2). The pattern also exhibited reflections that are assignable to rutile SnO₂ from the FTO substrate. Importantly, we did not observe any secondary phases of BiVO₄ or bismuth or vanadium oxide phases. The BiVO₄ films were (30 ± 1) nm thick, as determined by optical spectra and reported absorption coefficients for powder BiVO₄. We made photoanodes from these BiVO₄ films on FTO-glass slides such that the exposed active electrode area was circular to minimize electric field inhomogeneities (Figure 2b).

Figure 2. (a) XRD data (upper black line) of spin-coated BiVO₄ films on FTO-coated glass; fixed-slit intensities of monoclinic scheelite-type BiVO₄ (PDF 00-014-0688, black) and rutile SnO₂ (PDF 00-041-1445, blue) are depicted as vertical lines below. Photos of a neat BiVO₄ photoelectrode (b) and our [NiFe]-LDH nanocatalyst (c).

We integrated [NiFe]-LDH catalyst nanosheets with BiVO₄ photoanodes. The [NiFe]-LDH material contained 78% Ni(II) (relative to the total metal content) and was prepared as a dry nanoparticle powder (Figure 2c) which we suspended in water for drop-cast deposition on BiVO₄ photoanodes.

Optimization of Catalyst Mass Loading. Both, scheelite-type BiVO₄ and our [NiFe]-LDH nanocatalyst are yellow (Figure 2); optical spectra are shown in Figure S1. As both materials absorb light in the same spectral region, parasitic light absorption by the catalyst must be minimized. On the other hand, the availability of accessible catalytic sites must be maximized. Therefore, we optimized catalyst mass loading. We deposited [NiFe]-LDH catalyst nanosheets on BiVO₄ photoanodes with seven mass loadings between 1.1 and 20.0 µg cm⁻². We first established the PEC performance of each neat BiVO₄ photoanode in sulfite-containing buffered electrolyte (to obtain their photo-hole production ability), rinsed the electrodes well, dried them, applied catalyst, and measured photocurrent generation of these integrated [NiFe]-LDH–BiVO₄ photoanodes in sulfite-free buffered electrolyte. We defined a relative activity as the generated photocurrent density (jph) of the integrated catalyst–BiVO₄ photoanode obtained in sulfite-free electrolyte normalized to the photocurrent density of the neat BiVO₄ photoanode measured in sulfite-containing electrolyte:

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\text{relative activity} = \frac{j_{ph}(\text{with catalyst in neat buffer})}{j_{ph}(\text{without catalyst in buffer with sulfite})}
\]

The relative activity is a measure of how many photogenerated holes are utilized by the catalyst and can have values between 0 and 100%. Relative activities varied as a function of catalyst mass loading (Figure 3). The best catalyst mass loading we measured was 8.0 µg cm⁻², with a highest relative activity of (66 ± 2)%.

Figure 3. Average relative activities and their standard deviations of integrated [NiFe]-LDH nanocatalyst–BiVO₄ photoanodes as a function of catalyst mass loading. The red curve is the best exponentially modified Gaussian fit.

The observed mass-loading dependence (Figure 3) suggests that at low mass loadings the available number of electrocatalytic sites for water oxidation limits the relative activity. We propose that the increasing number of available catalytic sites can be approximated by a Gaussian function as catalyst mass on the surface rises linearly. Because we have a large ensemble of nanoparticles, and individual catalyst nanoparticles may randomly either be completely or not at all aggregated but are statistically more likely somewhere in between, approximation of the number of active sites by a Gauss curve is appropriate, i.e. the central limit theorem applies.

At high mass loadings, absorption of incident light by the catalyst nanoparticles becomes more dominant, and we obtained lower relative activities. Our observation of exponential behavior at high mass loadings suggests that Beer’s law governed light absorption as the amount of catalyst on the surface increased linearly. We found that an exponentially modified Gaussian fit function (convolution of a Gaussian with an exponential function) matched our data best. The maximum of this fit function was at 7.0 µg cm⁻², suggesting that we could achieve even slightly higher relative activity than the (66 ± 2)% we found at a catalyst mass loading of 8.0 µg cm⁻².

Linear-sweep voltammograms of BiVO₄ photoanodes are shown in Figure 4. We collected these current density vs applied potential curves under 100 mW cm⁻² of simulated 1 Sun AM 1.5G front-side illumination. Our BiVO₄ photoanodes exhibited expected PEC performance. We compared neat BiVO₄ photoanodes in sulfite-containing buffered electrolyte with integrated [NiFe]-LDH–BiVO₄ photoanodes with a nanocatalyst mass loading of 8.0 µg cm⁻² in sulfite-free aqueous pH 9.2 borate buffer. We found that under these conditions two thirds of all
photogenerated holes escaped loss processes. We also compared integrated [NiFe]-LDH-BiVO₄ photoanodes in 0.1 M borate buffer electrolyte with sulfite to neat BiVO₄ photoanode in buffered electrolyte without sulfite and found that integration with [NiFe]-LDH nanocatalysts enhanced photocurrent generation by a factor of 3.3 at the thermodynamic water oxidation potential.

Next, we wanted to know if addition of surfactants to aqueous nanocatalyst suspensions could enhance PEC performance. We aimed to find a surfactant that would (i) mitigate nanoparticle aggregation (cohesion between particles), and (ii) simultaneously lead to the most even distribution of nanoparticle catalysts on the BiVO₄ surface (governed by adhesion to the BiVO₄ surface).

**Choice of Surfactant.** We performed choice-of-surfactant experiments with Co₃O₄ water oxidation nanocatalysts on BiVO₄, which we made on FTO-glass substrates by electrodeposition, according to our earlier work. The precatalysts were ~2.5 nm diameter spinel Co₃O₄ particles, which we also developed in our group. Although the catalytic activity of Co₃O₄ is inferior to that of [NiFe]-LDH, both materials contain di- and tripositive first-row transition metals and are comparable for surfactant and aggregation studies.

We drop cast Co₃O₄ nanoparticles suspended in water without or with added surfactants (sodium dodecyl sulfate (SDS), benzoate, or citrate) onto BiVO₄ photoanodes, and assessed photocurrent generation. SEM images with EDS mapping of surface cobalt, vanadium (as proxy for BiVO₄), and carbon visualized distributions of the catalyst, particles and surfactants on the BiVO₄ surfaces. For comparability reasons, we measured PEC performance of the same electrode first without and then with catalyst, and observed the enhancement in photocurrent density at 1.23 V vs RHE (Figure 5). The catalyst mass loading was kept constant at 1.4 µg cm⁻² for all preparations. We obtained enhanced PEC performance from our integrated Co₃O₄–BiVO₄ photoanodes and surmised that further optimization was possible with reduced catalyst aggregation.

Surfactant-free Co₃O₄ nanoparticles showed substantial aggregation on the BiVO₄ surface. Addition of surfactant-free aqueous suspensions of Co₃O₄ nanoparticles increased the photocurrent density by a factor of 2.0 ± 0.2. Sodium citrate (2.5 mM) as surfactant increased the PEC performance by a factor of 2.6 ± 0.3. In contrast to that, addition of 5.0 mM SDS or sodium benzoate led to inferior photocurrent generation, yielding enhancement factors of only 1.2 ± 0.1 and 1.3 ± 0.2, respectively. We hypothesize that these results are a tradeoff between even distribution of Co₃O₄ nanoparticles on the BiVO₄ surface and agglomeration of the nanocatalyst by surfactant molecules, which block catalytic surface sites.

We turned to SEM imaging with EDS mapping to understand why citrate in the nanoparticle suspension led to the highest performance enhancement. Spectroscopic mapping of elemental X-ray lines gave spatial distributions of cobalt, vanadium, and carbon, which we analyzed along with their corresponding electron-images (Figure 6).
Choice of surfactant greatly affected the degree of aggregation of CoO nanoparticles on BiVO\textsubscript{4} photoanodes. Inspection of Co La\textsubscript{1} spatial distributions of SEM/EDS images (Figure 6a, green) shows that drop-casting aqueous CoO suspensions without added surfactant led to uneven catalyst distributions on the photoanode surface. Catalyst particles aggregated on vanadium-rich parts of the surface (Figure 6a, cyan). During the preparation of integrated photoanodes we noticed that aqueous CoO suspensions did not wet our BiVO\textsubscript{4} surfaces well. Nevertheless, the resulting photoanodes improved PEC performance by a factor of two compared to neat BiVO\textsubscript{4}.

Addition of surfactants to the nanoparticle suspensions did not always enhance PEC performance. SDS and sodium benzoate are monodentate ligands, whereas citrate is a capping agent that offers three binding sites. Integrated Co\textsubscript{3}O\textsubscript{4}–BiVO\textsubscript{4} photoanodes made from suspensions with SDS or sodium benzoate performed about the same as neat BiVO\textsubscript{4} and were inferior to neat CoO on BiVO\textsubscript{4}. Their SEM/EDS images (Figure 6b and c) indicate that in both cases dense blobs of surface carbon covered the surface; surfactant concentrations in the suspensions were virtually identical (5.0 mM). In case of SDS, the distribution of cobalt tracked with that of vanadium, whereas the carbon distribution was independent of both metals. In case of benzoate, we detected much less surface cobalt than vanadium, and we observed more carbon than vanadium. Apparently, sodium benzoate was able to bind very well to BiVO\textsubscript{4} and, as a result, less CoO was deposited. We hypothesize that SDS and benzoate detrimentally covered the integrated photoanodes. Large areas were coated by electrically insulating carbon (white areas in electron images, which arise from charging by the electron beam).

We obtained the best PEC performance enhancement with sodium citrate as surfactant. We added only 2.5 mM citrate to our nanocatalyst suspension to mitigate adverse carbon coating of our photoanodes. Figure 6d shows that less surface carbon was present compared to vanadium, and, most importantly, surface cobalt was evenly distributed, suggesting reduced aggregation of CoO nanoparticles.

Citrate forms stable complexes with dipositive metal ions, resulting in preferential chelation of Co(II) in CoO nanoparticles; BiVO\textsubscript{4} contains only tri- and pentapositive metal ions. Preferential ligation of cobalt is advantageous because (i) it reduces nanoparticle aggregation by decreasing inter-particle cohesion, and (ii) the attenuated binding of citrate to BiVO\textsubscript{4} prevents the formation of excessive carbon layers on BiVO\textsubscript{4}, which adversely affect catalyst adhesion and contact between catalyst and photoanode surface.

Now that we have established conditions to evenly spread nanocatalysts that contain dipositive transition metals on BiVO\textsubscript{4}, we applied our insights to integrated [NiFe]-LDH–BiVO\textsubscript{4} photoanodes.

**Effect of Citrate Surfactant or Isopropanol Dispersant on [NiFe]-LDH–BiVO\textsubscript{4} Photoanodes.** We added citrate to aqueous suspensions of [NiFe]-LDH nanocatalysts, analogous to experiments with CoO nanoparticles for integrated photoanodes; we also chose similar mass loadings (1.1 or 2.8 µg cm\textsuperscript{-2}). Addition of citrate enhanced PEC performance (relative to that of surfactant-free nanocatalysts) for both mass loadings, more so with less catalyst. Maximum relative activity was just above 60%, this time, however, with only a third of the catalyst amount than that needed without surfactants.

We obtained spatial distributions of [NiFe]-LDH nanosheets on BiVO\textsubscript{4} surfaces by SEM imaging with spectroscopic mapping of elemental X-ray lines of nickel, vanadium, and carbon (Figure 7). Inspection of Ni La\textsubscript{1} spatial distributions of SEM/EDS images (Figure 7a and b, green) shows that drop-casting aqueous [NiFe]-LDH nanosheet suspensions without added surfactant led to nanocatalyst aggregates on BiVO\textsubscript{4} surfaces. Drop-cast deposition of [NiFe]-LDH nanosheets from an aqueous suspension with 2.5 mM sodium citrate produced an even distribution of surface nickel, suggesting reduced aggregation (Figure 7c). Our results confirmed our hypothesis that citrate would decrease aggregation of CoO nanoparticles and [NiFe]-LDH nanosheets; both materials contain dipositive transition metal ions, which citrate preferentially chelates.\textsuperscript{[19]} The distribution of surface carbon was less even than that of nickel and vanadium, in line with our observations for CoO nanoparticles on BiVO\textsubscript{4} that were deposited from aqueous citrate-containing suspension.

Because surfactants ligate catalytic surface sites, we explored dispersants to spread nanocatalysts more evenly on BiVO\textsubscript{4} surfaces (Figure 8). Dispersants work by lowering the surface tension of the surfactant-free aqueous nanocatalyst suspension. Lower alcohols are well miscible with water. Addition of alcohol to aqueous nanoparticle-containing droplets has been reported to create a strong recirculating flow (Marangoni effect) and homogenize nanoparticle concentration within the droplet.\textsuperscript{[20]}

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**Figure 7.** SEM electron images (gray) with EDS mapping of the same area of surface nickel (green), vanadium (cyan), and carbon (orange). [NiFe]-LDH nanosheet aqueous suspensions were drop cast onto BiVO\textsubscript{4} electrodes, (a) without added surfactant, 2.8 µg cm\textsuperscript{-2} catalyst mass loading, (b) without added surfactant, 5.2 µg cm\textsuperscript{-2} catalyst mass loading, (c) with 2.5 mM sodium citrate, 2.8 µg cm\textsuperscript{-2} catalyst mass loading, and (d) without added surfactant but with 3.0 µL isopropanol dispersant, 5.2 µg cm\textsuperscript{-2} catalyst mass loading. The scale bar is 15 µm.
Droplets of aqueous [NiFe]-LDH nanocatalyst suspension did not wet the surface of our spin-coated BiVO₄ films well; droplets sat perched on the electrode surface (Figure 8c). We found that isopropanol wetted the BiVO₄ surface very well. When we added small amounts of isopropanol to the aqueous nanocatalyst-suspension droplet perched on the BiVO₄ surface, we noticed that the droplet dispersed very rapidly across the BiVO₄ surface. SEM/EDS images indicate that dispersion of a droplet of aqueous [NiFe]-LDH nanocatalyst suspension with isopropanol produced an even distribution of surface nickel with larger aggregates (Figure 7d).

The dispersant-to-suspension volume ratio mattered. We pipetted 3 or 6 µL isopropanol onto a 4.5 µL droplet of aqueous LDH-catalyst suspension (5.1 µg cm⁻² mass loading) perched on a BiVO₄ electrode and assessed PEC performance. We observed the suspension droplet rapidly spread across the entire electrode area, as expected. We did not obtain significantly better PEC activity with isopropanol as dispersant relative to surfactant-free LDH-catalyst suspension. We observed relative activities of (62 ± 7), (64 ± 3), or (62 ± 1) %, for catalyst deposition without, with 3 µL, or 6 µL isopropanol, respectively. The lower standard deviations found for deposition with isopropanol suggest homogenizing of nanocatalyst particles on the BiVO₄ surface, consistent with SEM/EDS data (Figure 7d).

**Figure 8.** Relative activities of integrated [NiFe]-LDH-BiVO₄ photoanodes prepared with isopropanol as dispersant, (a) as a function of the volume V of added isopropanol, (b) as a function of catalyst mass loading. Also depicted are photos of BiVO₄ photoanodes with aqueous [NiFe]-LDH-nanocatalyst suspension before (c) and after (d) dispersion by isopropanol.

**Conclusions**

We prepared integrated [NiFe]-LDH nanocatalyst-BiVO₄ photoanodes by drop casting surfactant-free [NiFe]-LDH nanosheets onto BiVO₄ films from aqueous suspensions. We identified the optimal mass loading for [NiFe]-LDH nanosheets on BiVO₄ photoanodes as 7.0 µg cm⁻² and reached photocurrents in buffered electrolyte without sacrificial agents that were only 34 % below those of neat BiVO₄ in a similar electrolyte with an added sacrificial hole acceptor. Our results show that catalyst mass loading is a tradeoff between maximized number of available catalytic sites and parasitic light absorption. We found that citrate surfactant, which preferentially ligates dative metals, enhanced photocurrent generation more than SDS or benzoate surfactants. SEM imaging with EDS mapping established that citrate led to the most even distribution of nanocatalysts, whereas photoanodes prepared with the other surfactants exhibited much aggregation or had little catalyst on the BiVO₄ surface. Use of citrate surfactant in the preparation of [NiFe]-LDH–BiVO₄ photoanodes allowed us to use only a third of the mass loading compared to preparations without surfactants to reach highest relative activities. Addition of isopropanol dispersant during [NiFe]-LDH nanosheet deposition reduced variability in relative activity, without affecting the mean relative activity. Our systematic optimization strategies for integrated catalyst–photoanode assemblies made from earth-abundant, robust materials provide a path towards functional artificial photosynthesis devices.

**Experimental Section**

**Materials and Methods**

Nanocatalysts were prepared at the Beckman Institute Laser Resource Center at the California Institute of Technology. PEC experiments were performed at the Molecular Materials Research Center (Beckman Institute at Caltech). SEM images were collected at the California Institute of Technology GPS Division Analytical Facility. All chemicals were purchased in the indicated grade and used as received. All water used in this work was of high purity and obtained from a Barnstead Diamond Nanopure system with a resistivity of ≥ 16 MΩ cm. Data analysis, unless otherwise noted, and graphing were performed with Igor Pro 6.37 (WaveMetrics, Inc.).

**Preparation of Integrated Catalyst–BiVO₄ Photoanodes**

Integrated [NiFe]-LDH–BiVO₄ photoanodes were prepared from spin-cast BiVO₄ films on ~ 3 cm × 10 cm FTO-glass substrates, with an area of the FTO slide masked with Scotch tape to provide bare FTO for electrical contact. The precursor solution was prepared similarly to a published procedure.[32] (i) 398 mg of vanadyl bis(acetylacetonate) were dissolved in 50.0 mL of 2.4-pentanediol (Sigma-Aldrich, ≥98%) by sonicating for 10 minutes to prepare a 30 mM solution; (ii) 728 mg of bismuth(III) nitrate pentahydrate were dissolved in 7.5 mL of 2.4-pentanediol by sonicating for 10 minutes to prepare a 200 mM solution; (iii) the vanadium and bismuth solutions were mixed to form the solution of 26 mM vanadyl bis(acetylacetone) and 26 mM bismuth(III) nitrate pentahydrate in 2,4-pentanediol. Slides were spin-coated for 9 cycles. A spin-coating cycle consisted of two times pipetting 200 µL of precursor solution onto the slide and allowing it to spread to cover the entire surface, spinning the slide at 1,000 rpm for 6 seconds. After that the slide was placed in a kiln at 500 °C for 10 minutes in ambient air. After the 9th cycle, the slides were annealed for 2 hours at 500 °C in ambient air. For best reproducibility, slides were allowed to slowly cool in ambient air after each cycle. To ensure comparability, the same BiVO₄ photoanodes were tested without and with catalyst; this way, the effect of BiVO₄ preparation differences on photocurrent generation was excluded. The catalyst particles we used are small compared to any BiVO₄ grain sizes we made, allowing relative PEC performance assessments. Integrated Co₃O₄–BiVO₄ photoanodes for choice-of-surfactant experiments were prepared from BiVO₄ films by electrodeposition from 35 mM VOSO₄, 10 mM Bi(NO₃)₃, and 80 mM NaI in aqueous nitric acid solution, according to our earlier work.[44]
FTO slides with BiVO₄ films were subdivided by scribing and breaking them into ~1.0 cm x 2.5 cm pieces. All electrodes had some bare FTO, to which a silver-coated copper wire was firmly attached with silver paint (SPI, high purity). For mechanical stability the wire was run inside a glass tube, whose end and all exposed conducting parts were sealed with an epoxy adhesive (Loctite Hylsec 9460). To obtain the same defined area of exposed BiVO₄ (0.079 cm² for photoanodes to have CoO₂ catalyst deposited on them and 0.179 cm² for photoanodes to have [NiFe]-LDH catalyst deposited on them) on each electrode, part of the BiVO₄ film was masked with a 3.2-mm or 4.8-mm diameter metal disk, respectively, and spray-painted with black high-temperature paint (McMaster-Carr). We tested the chemical stability of this paint in our electrolytes and confirmed that it was stable for hours, which was much longer than the measurement time.

Prior to catalyst deposition, the PEC performance of the neat BiVO₄ photoanodes was assessed using the PEC procedures described below. Integrated CoO₂–BiVO₄ photoanodes were prepared by drop-casting 0.2 mg mL⁻¹ aqueous suspension of CoO₂ nanoparticles onto BiVO₄ photoanodes. Mass loadings of 0.7, 1.4, or 2.9 µg cm⁻² were prepared by pipetting droplets of 2.5, 5.0, or 10.0 µL, respectively, onto the photoanode surface. Droplets were spread across the photoanode surface using the pipette tip. Placing the catalyst–photoanode photoanodes under an infrared lamp for 10 minutes evaporated the remaining liquid. Additional integrated CoO₂–BiVO₄ photoanodes were prepared by drop-casting 5.0 µL of 0.2 mg mL⁻¹ aqueous CoO₂ suspensions that also contained 2.5 mM sodium citrate, 5.0 mM sodium dodecyl sulfate, or 5.0 mM sodium benzoate. Integrated [NiFe]-LDH–BiVO₄ photoanodes were fabricated by drop-casting 0.2 mg mL⁻¹ aqueous suspension of [NiFe]-LDH nanosheets onto BiVO₄ photoanodes. Mass loadings of 1.1, 2.8, 5.1, or 8.0 µg cm⁻² were achieved by depositing droplets of 1.0, 2.5, 4.5, or 7.2 µL, respectively, onto a photoanode area of 0.179 cm² using a micropipette, spreading the droplet around the photoanode surface with the pipette tip, and then evaporating the remaining liquid by placing the catalyst–BiVO₄ photoanodes under an infrared lamp for 30 minutes. Mass loadings of 10.0, 15.0, or 20.0 µg cm⁻² were obtained by sequentially depositing two drops of 4.5, 6.7, or 9.0 µL, respectively, spreading the droplet around the photoanode surface with the pipette tip, and then evaporating the remaining liquid after each drop. Integrated [NiFe]-LDH–BiVO₄ photoanodes were prepared using either citrate as surfactant or isopropanol as dispersant during drop casting. Droplets of 1.0 or 2.5 µL of aqueous [NiFe]-LDH suspension with 2.5 mM sodium citrate were placed on photoanodes with a surface area of 0.179 cm² using a micropipette, spreading the droplet around the photoanode surface with the pipette tip, and then drying the photoanodes under an infrared lamp for 10 minutes to achieve mass loadings of 1.1 to 2.8 µg cm⁻², respectively. Droplets of 2.5 or 4.5 µL were placed on photoanodes to obtain mass loadings of 2.8 or 5.1 µg cm⁻², respectively. Adding 3.0 or 6.0 µL of isopropanol dispersed the droplets; placing the catalyst–BiVO₄ photoanodes under an infrared lamp for 10 minutes evaporated the remaining liquid.

Physical Characterization

We collected XRD data with a Bruker D2 PHASER diffractometer with monochromatic Cu Kα radiation (1.5418 Å; tube power 30 kV, 10 mA). The resolution was 0.05° in 2θ, and the counting time was 3 s per step. We used a custom-built acrylic sample holder to place the sample at the correct height in the instrument. We conducted XRD pattern analysis with the Bruker DIFFRAC.SUITE software coupled to the International Centre for Diffraction Data powder diffraction file database (ICDD, PDF-2 Release 2012).

We measured optical spectra of scheelite-type BiVO₄ and our [NiFe]-LDH nanosheets to evidence that both yellow materials absorbed light in the same spectral region. The BiVO₄ films on FTO-glass were sufficiently transparent to obtain the optical spectrum in transmission mode on a Cary 50 Bio spectrophotometer with bare FTO-glass as background. The [NiFe]-LDH catalyst nanosheets were a dry powder, and we collected the optical spectrum in reflectance mode, using a fibre-optic Ocean Optics HR2000CG-UV-NIR spectrometer, an Ocean deuterium lamp, and a LabSphere Spectralon certified reflectance standard. Conservation of energy dictates that the sum of absorption a, reflection r, and transmission t, at the wavelength λ account for all the incident radiation: a+ r+ t = 1. In opaque samples, the transmission t, approaches 0, hence the measured low reflectance of [NiFe]-LDH nanosheets in the ultraviolet spectral region corresponds to a high absorbance (Figure S1).

We obtained morphologies and concomitant elemental distributions from SEM images with EDS mapping. We used a Zeiss LEO 1550VP Field-Emission SEM coupled to an Oxford X-Max SDD X-ray Energy Dispersive Spectrometer, which allowed quantitative elemental analysis with a relative accuracy of better than 5% and detection limit of better than 0.5%. EDS maps were acquired using the AZtec software package. We fixed photoanode substrates to the sample stage with carbon tape (EMS), which was wrapped around to the top of each sample to minimize charging effects.

Photoelectrochemistry

Linear sweep voltammograms of neat BiVO₄ and BiVO₄ with [NiFe]-LDH catalysts on FTO-glass electrodes were collected with a Princeton Applied Research model 362 potentiostat at room temperature and in ambient air (scan rate 10 mV s⁻¹). Electrochemical experiments were carried out in a standard Pyrex three-electrode single compartment electrochemical cell equipped with a flat quartz window for illumination. All potentials reported here are relative to the reversible hydrogen electrode (RHE). For integrated [NiFe]-LDH–BiVO₄ photoanodes, we studied PEC performance in 0.1 M (pH 9.2) borate buffer electrolyte. To assay the catalyst’s role in photocurrent generation, we first measured photocurrents of neat BiVO₄ photoanodes in 0.1 M (pH 9.2) borate buffer with 0.25 M Na₂SO₃, then thoroughly washed them with water, and lastly tested them with catalyst in electrolyte without sulfite. After each photoanode was tested in borate buffer with sulfite, the photoelectrochemical cell was washed and filled with new electrolyte. Borate buffer was prepared by adding boric acid (Sigma-Aldrich, 99%) to a solution of 15.24 g Na₂B₄O₇·10H₂O (Sigma-Aldrich, ≥99.5%) in 400 mL water until pH 9.2 was reached. For integrated CoO₂–BiVO₄ photoanodes, PEC performance was examined in 0.1 M (pH 13.0) aqueous KOH electrolyte. To assess the catalyst’s role in photocurrent generation, we first investigated neat BiVO₄ photoanodes in 0.1 M (pH 13.0) aqueous KOH with 0.5 M Na₂SO₃ (J.T.Baker, >99%), then thoroughly washed them with water, and lastly tested them with catalyst in electrolyte without sulfite.

All current density versus potential data were collected with rapid stirring of the liquid, to minimize mass transport effects and remove nucleated bubbles from the electrode surface; the data were not corrected for any uncompensated resistance losses. A Ni gauge (Alfa) counter electrode was used. In pH 9.2 electrolyte, the reference electrode was a calibrated 3 M NaCl Ag/AgCl electrode (BASi), whereas a calibrated 0.1 M KOH Hg/HgO electrode (CH Instruments) served as the reference electrode in pH 13 electrolyte. We measured photocurrents with a setup described elsewhere. Briefly, an Ocean Instruments model 66902 halogen light source with an ozone-free bulb supplied simulated sunlight; an AM1.5G filter was placed between the lamp and the photoelectrochemical cell. Electrodes were stable for at least three scans. Photocurrent values were averaged using three electrodes per BiVO₄ preparation, in supporting
Acknowledgements

We thank Chi Ma and June Wicks for help with SEM imaging and EDS mapping, and George Rossman for help with reflectance measurements. Research was carried out in the Laser Resource Center and the Molecular Materials Research Center of the Beckman Institute of the California Institute of Technology. T.S.S. acknowledges the Caltech SURF office, a Dr. Terry Cole SURF Fellowship, and a Jack and Edith Roberts SURF Fellowship.

Keywords: artificial photosynthesis • integrated photoanodes • bismuth vanadate • earth-abundant nanocatalysts • solar water oxidation


We integrated laser-synthesized [NiFe]-layered double hydroxide nanocatalysts with BiVO₄ photoanodes, optimized catalyst mass loading, and mitigated nanoparticle aggregation. Our systematic optimization strategies led to enhanced photoelectrochemical performance.