Supporting Information

for

Cobalt Hexacyanoferrate on BiVO₄ Photoanodes for Robust Water Splitting

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1. **Catalyst modification of photoanodes**

In order to modify BiVO$_4$ photoanodes with the CoFe-PB catalyst, different methods were considered, namely electrodeposition, dip-coating in CoFe-PB nanoparticle dispersion, and sequential dip-coating in reactant Co$^{2+}$ and [Fe(CN)$_6$]$^{3-}$ solutions.

Electrodeposition, which has led to high water oxidation efficiencies in electrocatalysis, was envisaged but caused deactivation of the underlying photoanode, as shown in Figure S1a. For coating the film with nanoparticles, CoFe-PB was prepared by slowly dropping (< 1 drop/5s) an aqueous solution of 0.02 M K$_3$[Fe(CN)$_6$] into 0.04 M CoCl$_2$ in H$_2$O. BiVO$_4$ photoanodes were left in 30 mL dispersions of 100 and 150 mg of nanoparticles under stirring for 3-5 days. The resulting photoelectrochemical behaviour is akin to sequentially coated BiVO$_4$ anodes. (see Figure S1b) Nonetheless, the nanoparticles are likely to be only electrostatically attached to the BiVO$_4$ surface and hence may fall off over time.

![Figure S1: Cyclic voltammograms (50 mV/s) under chopped light (1Hz, 100 mW·cm$^{-2}$) of BiVO$_4$ photoanodes in 0.1 M KPi (pH 7) buffer solution a) before and after applying the electrodeposition method, and b) after dip-coating for 3 days in 100 mg and 150 mg CoFe-PB nano-particle dispersions.](image)

Consequently, we preferred the sequential coating method, which is described in the main text. Various repetitions of the sequential coating cycle were carried out. As shown in Figure S2, it is necessary to repeat the sequence at least four times to reach maximum photocurrent enhancement. After 4 repetitions, generally, no further activity increase was observed.
Figure S2: Cyclic voltammograms (50 mV/s) under chopped light (1Hz, 1sun) of BiVO$_4$ photoanodes in 0.1 M KPi (pH 7) buffer solution modified with CoFe-PB by a) 3x, b) 4x, c) 5x repetitive sequential coating.

The following synthetic mechanism is assumed. When dipping BiVO$_4$ in the [Fe(CN)$_6$]$^{3-}$ precursor solution, the iron cyanide complexes bind with the negatively charged N site of the CN-ligand to uncoordinated metal ions on the BiVO$_4$ surface, namely to vacant Bi sites. (The more stable low-index surfaces of BiVO$_4$ expose coordinatively unsaturated BiO$_x$ units, but not V sites.). After subsequent dipping in a Co$^{2+}$ solution, the cobalt ions can bind to vacant CN sites (at the N site). Repeating the sequence, three-dimensional CoFe-Prussian blue complexes are formed on the surface.
2. Electron microscopy and microanalysis

2.1. SEM analysis

Figures S3 a and b show Scanning Electron Microscopy (SEM) images of the pristine nanostructured BiVO₄ surface before (S3a) and after (S3b) electrochemical treatment (1h at 1.23 V vs RHE under 1 sun light irradiation). It seems that this electrochemical treatment softens the edges of the nano-crystallites, but no substantial change of the morphology occurs. Figures S3c and d show SEM images of catalyst modified samples CoFe-PB/BiVO₄, also before (S3c) and after (S3d) electrochemical treatment. All surfaces have similar structures and morphologies; the catalyst modification is only barely visible.

Figure S3: SEM images of a) freshly prepared and b) electrochemically treated BiVO₄, and c) freshly prepared and d) electrochemically treated CoFe-PB/BiVO₄.

Figure S4 shows SEM images of the cross-sections of CoFe-PB/BiVO₄ (S4a and d) and corresponding microanalysis with Energy Dispersive X-Ray Spectroscopy (EDS). Fine-focusing on the surface is necessary in order to detect the catalyst components cobalt and iron. The amount of Co and Fe at the surface is around 1% with a slightly higher percentage recorded for Co than for Fe. The detected Bi, V and O amounts correspond well to the theoretical Bi:V:O ratio of 1:1:4 of stoichiometric BiVO₄. Absolute values,
however, have to be taken with extreme caution, especially for those small quantities (<5 %). They depend on the peak integration and may vary enormously, if certain elements are included or omitted in the count.

Figure S4: SEM images of the a) cross-sections (S4a and S4d) of untreated CoFe-PB/BiVO$_4$ with corresponding EDS spectra (S4c and S4f) and elemental compositions (S4b and S4e).
2.2. TEM analysis

High-Resolution Transmission Electron Microscopy (HR-TEM) was carried out in combination with EDS detection of highly focused parts of the substrate nanoparticles.

![HR-TEM images and EDS spectra](image)

**Figure S5:** HR-TEM images (left, a-f) and corresponding EDS microanalysis (right, in atomic %) of scratched CoFe-PB/BiVO₄ with red circles showing the amorphous CoFe-PB phase and green circles crystalline BiVO₄. When the amorphous particle is very small, its EDS spectrum still yields a significant amount of Bi and V due to the spatial resolution limit of the EDS technique.

As seen in **Figure S5**, an amorphous phase is formed at some parts of the BiVO₄ surface, especially on corners and edges. With highly focused EDS detection, this phase can be analysed. It contains mainly Co and Fe in ratios around 1:1 and, therefore, is attributed to the CoFe-PB catalyst. The small nanocrystalline surface formations, such as in **Figure S5a** (green circle), can clearly be identified to be BiVO₄ alone, without containing CoFe-PB constituent elements. The bulk bismuth vanadate contains Bi and V in the ideal Bi:V ratio of around 1:1. However, at some places, especially at the nanostructured surface, Bi appears to be in excess, due to VO₄ vacancies (both V and O contents are diminished), resulting in positively doped BiVO₄. The lattice spacing of BiVO₄, as seen in **Figure S6**, was measured to lie between 0.28 and 0.31 nm, corresponding to the (-121) and (040) planes respectively, which confirms the monoclinic scheelite structure."
Figure S6: HR-TEM images with analysis of the lattice spacing of nanostructured monoclinic scheelite BiVO$_4$. 

0.28 nm

0.31 nm
3. XPS

Different electrodes were analysed by X-ray Photoelectron Spectroscopy (XPS) in order to obtain information about surface structure and possible changes of electronic coordination before and after electrochemical treatment. Obtained atomic ratios of surface atoms (2-3 nm penetration depth of X-Rays) are given in Table S1.

Table S1: Atomic percentages detected by XPS on the surface of different (fresh and electrochemically treated) CoFe-PB/BiVO₄ electrodes. (n.d. = not detected; n.a. = not analysed / not taken into account in the analysis)

| Investigated electrodes | Bi  | V   | Co  | Fe* | K   | N   | C   | O   | Sn |
|-------------------------|-----|-----|-----|-----|-----|-----|-----|-----|----|
| atomic percent          | %   | %   | %   | %   | %   | %   | %   | %   | %  |
| bare BiVO₄ (fresh)      | 7.4 | 5.7 | -   | -   | 2.3 | n.d.| 42.5| 44.8| n.d.|
| bare BiVO₄ (fresh)      | 11.5| 4.7 | -   | -   | 3.2 | n.d.| 41.8| 45.0| n.d.|
| bare BiVO₄ (fresh)      | 9.6 | 5.2 | -   | -   | n.a.| 4.1 | 23.6| 48.8| 9.3 |
| x4-CoFe-PB/BiVO₄ (fresh)| 3.9 | 2.6 | 5.5 | 3.1 | n.a.| 8.9 | 33.9| 40.5| 1.7 |
| x6-CoFe-PB/BiVO₄ (fresh)| 2.1 | 1.8 | 3.2 | 1.5 | 2.2 | 14.6| 53.6| 18.8| 0.3 |
| x8-CoFe-PB/BiVO₄ (fresh)| 7.1 | 4.9 | 1.1 | 1.9 | 24.1| 4.6 | 38.4| 37.0| 1.6 |
| x4-CoFe-PB/BiVO₄ (2h CA)| 4.3 | 4.3 | 1.3 | n.d.| n.a.| 3.5 | 16.8| 19.8| 7.1 |
| x6-CoFe-PB/BiVO₄ (5 CVs)| 3.5 | 3.3 | 0.3 | n.d.| 18.8| 0.8 | 22.7| 44.8| 0.7 |
| x6-CoFe-PB/BiVO₄ (various PEC studies)| 3.2 | 1.4 | 1.4 | 1.1 | 3.6 | 9.9 | 38.6| 38.3| 0.4 |

* Fe amounts have to be regarded with caution, since the Fe 2p peaks overlap with the Sn 3p₃/₂ (from the FTO substrate) and cannot be clearly deconvoluted. In some cases, indeed, the detection of Fe was impossible due to the Sn 3p₃/₂ peak.

As also seen from EDS/TEM analysis, the surface contains a higher amount of Bi than V. The surface-sensitive XPS measurement gives an average Bi:V ratio of 1.6, in agreement with a recent mechanistic study about BiVO₄ photoanodes.¹ There is no significant change in the Bi:V ratio before and after different photoelectrochemical
treatments. From XPS alone no rational conclusion can be drawn about the Co:Fe ratio on the surface, as the Fe 2p\(_{3/2}\) peak overlaps with Sn 3p\(_{3/2}\), which hampers deconvolution of the peaks. However, as a general trend, a higher Co than Fe content can be seen, which is in agreement with data from EDS/TEM. Representative XPS spectra of bare BiVO\(_4\), treated and untreated CoFe-PB/BiVO\(_4\) are shown for each spectral range of metal constituent atoms. (Figures S7 - S11).

**Figure S7:** XPS spectrum surveys (complete range) of a) bare BiVO\(_4\) and b) CoFe-PB/BiVO\(_4\)
Figure S8: XPS spectrum of the Fe 2p range of a) fresh and b) treated CoFe-PB/BiVO₄
Figure S9: XPS spectrum of the Co 2p range of a) fresh and b) treated CoFe-PB/BiVO₄ and c) Co₃O₄ for comparison. The presence of adventitious CoOₓ on the sample should include the appearance of a typical dominant peak below 780 eV.2-4
Figure S10: XPS spectrum of the Bi 4f of a) fresh and b) treated BiVO₄ and CoFe-PB/BiVO₄. CoFe-PB modification does not change the Bi spectral signature.
Figure S1: XPS spectrum of the V 2p range of the BiVO₄ and CoFe-PB/BiVO₄. The V peak remains unaltered by CoFe-PB coating and electrochemical treatment.

In those spectra where Fe 2p could be clearly detected, a clear, signature peak at 708.3 - 708.4 eV prevails and does not show a remarkable difference before and after photoelectrochemical treatment (Figure S8). This binding energy corresponds to Fe(II) as in [Fe(CN)₆]⁴⁻. In those spectra where Fe 2p could be clearly detected, a clear, signature peak at 708.3 - 708.4 eV prevails and does not show a remarkable difference before and after photoelectrochemical treatment (Figure S8). This binding energy corresponds to Fe(II) as in [Fe(CN)₆]⁴⁻.

Cobalt (Co 2p) features lie between 780 - 789 eV and do not show a remarkable difference before and after treatment (Figure S9). Although Co binding energies cannot clearly be deconvoluted, a maximum peak around 780-781 eV is attributed to Co(III) in the structure. We assume Co to be partly coordinated to cyanide nitrogen, partly to oxygen of H₂O or BiVO₄ on surface. The lack of Co peaks below 780 eV, typical of CoOₓ, is an additional support for the absence of adventitious oxide species on these electrodes.

Bismuth (Bi 4f₇/₂) shows a peak at 158.5 - 159.0 eV (Figure S10) binding energies, which corresponds to Bi(III) in the BiVO₄. The strong vanadium 2p₃/₂ peak at 516.0 - 516.7 eV in all spectra can clearly be attributed to vanadium (IV) oxide as present in the BiVO₄ structure (Figure S11).

An interesting artifact can be observed in the case of bismuth. When the electrodes undergo a long photoelectrochemical treatment, this Bi 4f peak broadens, extending to higher binding energies. It can be deconvoluted to a second peak at slightly higher binding
energy (159.5 - 159.7 eV), which may be due to Bi$_2$O$_3$ or similar structures that form during the experiment (Figure S10).
4. IR

Infrared spectroscopy was carried out in order to further confirm the presence of the cobalt hexacyanoferrate complex. (Figure S12). The characteristic CN stretches at frequencies around 2070-2150 cm\(^{-1}\) (depending on the metal oxidation state) are unique and cannot be attributed to any other non-cyano compound. Therefore, their appearance is a strong indicator of the presence of iron cyanide on the surface.

For the FT-IR measurement, the substrate was scratched from several electrodes and pressed as a KBr disk. Due to its very small concentration (< 1 %) the peak around 2100 cm\(^{-1}\) is very weak, thus rendering the distinction between differently coordinated cyanides on the surface impossible.

Figure S12: (a) FT-IR spectra of KBr disks of scratched electrode material (bare BiVO\(_4\), black, and CoFe-PB/BiVO\(_4\), red) of the complete range and (b) of the cyanide stretching region between 1800 and 2300 cm\(^{-1}\) to identify the characteristic CN stretch of the metal hexacyanoferrate complex.
5. **Estimation of photovoltage**

From the measured equilibrium potentials, the open circuit voltage \((OCV)\), with no applied external bias, the photovoltage \(V_{Ph}\) can be estimated as:

\[
V_{\text{Photo}} = OCV \,(\text{dark}) - OVC \,(\text{light})
\]  

\[(S1)\]

From **Figure S13** it can be seen that the photovoltage increases significantly with catalyst deposition. In similar systems, this behavior has been ascribed to passivation of surface states and release of Fermi level pinning at the semiconductor liquid interface.\(^7,8\)

**Figure S13**: Equilibrium open-circuit voltage (OCV) measured for bare BiVO\(_4\) and CoFe-PB/BiVO\(_4\) in the dark (black) and under light (red) and determined corresponding photovoltage \(V_{\text{photo}}\).
6. UV-Vis absorption spectroscopy

The UV-Vis absorbance of the electrodes was determined by recording both transmittance (with FTO glass as reference) and diffuse reflectance, and then converting to absorbance, using the relation:

\[ A = -\log(T + R) \]  \hspace{1cm} (S2)

The bandgap was subsequently determined by fitting the absorbance data with the Tauc method to a direct transition:

\[ (h\nu)^2 = C(h\nu - E_g) \]  \hspace{1cm} (S3)

with the absorption coefficient \(\alpha = A*l\) (determined by the layer thickness \(l\)) and with \(C\) being the proportionality constant. It has to be noted that actually BiVO\(_4\) is an indirect semiconductor but its bandgap lies very close to the experimentally observed direct, allowed absorption,\(^{10,11}\) which facilitated fitting according to equation (S3).

UV-Vis spectroscopy showed no distinguishable influence of CoFe-PB on the absorption, as can be seen in Figure S14. The broad absorption band of CoFe-PB absorption (see inset of Figure S14a) at around 2.3 - 2.5 eV cannot be detected. Its intensity is negligible compared to that of BiVO\(_4\), since the CoFe-PB:BiVO\(_4\) ratio is much less than 1%. The fitted bandgap (Figure S14b) lies between 2.40 and 2.45 eV (accounting for the fitting inaccuracies), which is in good agreement with the literature,\(^{12}\) and is not influenced by the CoFe catalyst.

![Figure S14](image_url)

**Figure S14:** (a) UV-Vis Absorption spectra and (b) Tauc fitting of bare BiVO\(_4\) (black) and CoFe-PB modified BiVO\(_4\) (red). The UV-Vis absorption spectrum of powdered CoFe-PB is shown in Figure S14a as inset.
7. IPC

The supernatant buffer solutions were analysed by inductively coupled plasma optical emission spectrometry (IPC-OES) for traces of the electrode materials Bi, V, Co and Fe, as well as of other trace metals (Al, Cr, Cu, Mn, Ni, Zn). The electrodes were treated differently and had different catalyst coatings. (See Table S2 and Table S3)

No significant amount of metal ions could be detected, while the small detected amounts seem to vary arbitrarily for differently treated electrodes, so that no clear trend can be observed. A slightly higher Fe content might be due to traces of Fe in the solvent. Also traces of Al, Zn and Cr could be detected, with (for Al and Zn) even higher concentrations than substituent elements. (< 8 mmol Al. < 0.5 mmol Zn. < 0.06 mmol Cr). Traces of Co and Fe were also detected in the supernatant solution of bare BiVO₄, hence it cannot clearly be described as catalyst loss. Hence, we conclude that the catalyst is stable and not washed into solution.
Table S2  Trace metal quantities in mg/l, detected by ICP-OES, for differently treated BiVO₄ photoanodes in supernatant KPi (0.1 M) buffer solution with V = 30 mL. (n.d. = not determined; n.a. = not analysed)

| Detected elements | Bi  | V  | Co | Fe  | Al  | Zn  | Cr  |
|-------------------|-----|----|----|-----|-----|-----|-----|
| units             | mg/l| mg/l|mg/l|mg/l|mg/l|mg/l|mg/l|
| bare BiVO₄ (multiple CV) | 0.17| 0.12|n.d.|0.22|0.76|0.12|n.d.|
| bare BiVO₄ (multiple CV) | n.d.| n.d.|n.d.|n.d.|0.69|0.16|n.d.|
| bare BiVO₄ (40CVs) | n.d.| n.d.|0.41|0.5 |1.16|0.06|0.72|
| x2-CoFe-PB/BiVO₄ (10 CVs) | n.d.| n.d.|n.d.|0.64|n.a.|n.a.|n.a.|
| x4-CoFe-PB/BiVO₄ (10 CVs) | n.d.| n.d.|0.04|0.12|2.31|0.04|0.07|
| x4-CoFe-PB/BiVO₄ (40 CVs) | 0.11| n.d.|n.d.|0.42|n.a.|n.a.|n.a.|
| x5-CoFe-PB/BiVO₄ (100 CVs) | 0.2 | n.d.|n.d.|0.64|n.a.|n.a.|n.a.|
| x5-CoFe-PB/BiVO₄ (100 CVs) | n.d.| n.d.|0.02|1.07|2.27|0.09|0.07|
| x6-CoFe-PB/BiVO₄ (5 CVs) | n.d.| n.d.|0.46|0.44|0.98|0.07|       |
| x6-CoFe-PB/BiVO₄ (10 CVs) | n.d.| 0.09|0.07|1.03|2.29|0.04|0.07|
| x6-CoFe-PB/BiVO₄ (40 CVs) | 0.11| n.d.|n.d.|0.42|n.a.|n.a.|n.a.|
| x6-CoFe-PB/BiVO₄ (2h CA) | n.d.| 0.43|0.47|1.1 |0.05|0.07|       |
| x6-CoFe-PB/BiVO₄ (EIS) | n.d.| n.d.|0.45|0.59|1.25|0.06|0.07|
| x8-CoFe-PB/BiVO₄ (EIS) | n.d.| n.d.|0.47|0.6 |1.26|0.07|0.76|

Table S3  Trace metal quantities in mmol, detected by ICP-OES, for differently treated BiVO₄ photoanodes in supernatant KPi (0.1M) buffer solution with V = 30 mL. (n.d. = not determined; n.a. = not analysed)

| Detected elements | Bi | V  | Co | Fe  | Al  | Zn  | Cr  |
|-------------------|----|----|----|-----|-----|-----|-----|
| units             | mmol| mmol|mmol|mmol|mmol|mmol|mmol|
| bare BiVO₄ (multiple CV) | 0.03| 0.08|n.d.|0.13|0.94|0.06|n.d.|
| bare BiVO₄ (multiple CV) | n.d.| n.d.|n.d.|n.d.|0.85|0.08|n.d.|
| bare BiVO₄ (40CVs) | n.d.| n.d.|0.23|0.30|1.43|0.03|0.46|
| x2-CoFe-PB/BiVO₄ (10 CVs) | n.d.| n.d.|n.d.|0.38|n.a.|n.a.|n.a.|
| x4-CoFe-PB/BiVO₄ (10 CVs) | n.d.| n.d.|0.02|0.61|2.85|0.02|0.04|
| x4-CoFe-PB/BiVO₄ (40 CVs) | 0.02| n.d.|n.d.|0.25|n.a.|n.a.|n.a.|
| x5-CoFe-PB/BiVO₄ (100 CVs) | 0.03| n.d.|n.d.|0.38|n.a.|n.a.|n.a.|
| x5-CoFe-PB/BiVO₄ (100 CVs) | n.d.| n.d.|0.01|0.64|2.80|0.05|0.04|
| x6-CoFe-PB/BiVO₄ (5 CVs) | n.d.| n.d.|0.26|0.26|1.21|0.00|0.04|
| x6-CoFe-PB/BiVO₄ (10 CVs) | n.d.| 0.06|0.04|0.61|2.83|0.02|0.04|
| x6-CoFe-PB/BiVO₄ (40 CVs) | 0.02| n.d.|n.d.|0.25|n.a.|n.a.|n.a.|
| x6-CoFe-PB/BiVO₄ (2h CA) | n.d.| n.d.|0.24|0.28|1.36|0.03|0.04|
| x6-CoFe-PB/BiVO₄ (EIS) | n.d.| n.d.|0.25|0.35|1.54|0.03|0.04|
| x8-CoFe-PB/BiVO₄ (EIS) | n.d.| n.d.|0.27|0.36|1.56|0.04|0.49|

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8. **Comparison of catalysts performance**

In order to compare catalytic efficiencies, the common water oxidation catalysts CoO$_x$ ("CoPi") and FeOOH were deposited on the BiVO$_4$ photoanodes. CoO$_x$ and FeOOH were chosen because the CoFe-PB system contains Co, as well as Fe atoms, which may both be believed to form (hydr-) oxide species, which in turn form the catalytic active phase.

Herein we refer to CoO$_x$ and CoPi (cobalt phosphate) interchangeably, as it is well-known that CoO$_x$ in KPi buffer is stabilized by phosphate in solution, forming the so-called "CoPi" catalytic active species. CoO$_x$ is prepared by two different methods, electrodeposition and dipcoating in Co$^{2+}$ solution. Electrodeposition was done in a solution of 0.5 mM Co(NO$_3$)$_2$ on 0.1 M KPi buffer (pH 7) in a three-electrode setup, with a BiVO$_4$ working electrode, Pt counter electrode and Ag/AgCl (3M KCl) reference and by applying a potential of 0.9 V (vs Ag/AgCl) for 500 and 900 seconds. For the dipcoating, the BiVO$_4$ electrode was dipped in a 0.1 M Co(NO$_3$)$_2$ (in H$_2$O) solution for four times five minutes. This experimental approach is akin to the preparation of CoFe-PB modified electrodes. The PEC enhancement reached by the different CoO$_x$/BiVO$_4$ systems in KPi buffer (pH 7) is very similar, and also it is alike the photoelectrochemical characteristics of CoFe-PB/BiVO$_4$ (**Figure 3a** in the main text). However, when performing the measurement in acetate buffer, the photocurrent decreases dramatically with number of subsequent CV scans (**Figure S15**). In CoO$_x$, Co$^{3+}$ is reduced to Co$^{2+}$ in neutral or acidic solution, which, the absence of phosphate, dissolves into solution.

FeOOH was photodeposited on BiVO$_4$, as described by Choi *et al.*$^{13}$ The modification of BiVO$_4$ with FeOOH improved the photocatalytic performance compared to bare BiVO$_4$, but showed inferior PEC characteristics compared to CoO$_x$ and CoFe-PB modified systems (**Figure 3a** in the main text).
Figure S15: Repetitive CVs (50 mV/s) under light (1sun illumination) of BiVO$_4$ photoanodes modified with CoO$_x$ in acetate buffer (pH 4.5). The blue curves decrease in current density with number of CV scans.
9. Calculation of the Faradaic efficiency

The Faradaic efficiency quantifies the efficiency of oxygen production, i.e. how much of the photogenerated charges, measured as photocurrent, are actually used for water oxidation. If all charges are transferred to water in order to create oxygen, the theoretical amount of oxygen \( n_{\text{theoretical}} \) can be determined by Faraday’s law and is given by:

\[
 n_{\text{theoretical}}(\text{mol}) = \frac{Il}{zF}
\]  

with \( I \) being the measured current, \( z \) being the number of transferred charges (i.e. \( z = 4 \) for water oxidation) and the Faraday constant \( F = 96485 \text{ C/mol} \).

The evolved oxygen that was measured by gas chromatography was converted into partial pressure by calibration of the chromatograph, and further transformed to a molar quantity \( n_{\text{evolved}} \) by assuming the ideal gas law and by taking into account the gas flux to the chromatograph:

\[
 n_{\text{evolved}} = \frac{p(O_2)/p^o}{V_m} \cdot (\text{total flux} \cdot \text{time})
\]  

with \( p(O_2)/p^o \) being the partial amount of oxygen gas, \( V_m \) the molar volume \( V_m = 22.4 \text{ mol/l} \) and the flux into the gas chamber being multiplied by time.

From this, the Faradaic efficiency can be calculated as:

\[
 FE(\%) = \frac{n_{\text{evolved}}(\text{mol})}{n_{\text{theoretical}}(\text{mol})} \cdot 100\%
\]  

10. Charge-transfer and charge-separation efficiencies

10.1. Charge-transfer efficiency

The charge-transfer efficiency \( \eta_{CT} \) of a system can be obtained by performing photoelectrocatalysis in a concentrated hole-scavenger solution, for which \( \eta_{CT} \) can be assumed to be 100%. The photocurrent density in water, or buffer, respectively, can be defined as:

\[
 j_{H_2O} = j_{\text{max}} \cdot \eta_{\text{absorption}} \cdot \eta_{CS} \cdot \eta_{CT}
\]  

with \( j_{\text{max}} \) being the maximum attainable photocurrent, \( \eta_{\text{absorption}} \) the light absorption efficiency, \( \eta_{CS} \) the charge-separation efficiency of excited electron-hole pairs and \( \eta_{CT} \) the charge-transfer efficiency, i.e. the efficiency of the effective surface catalysis.
While \( j_{\text{max}} \) and \( \eta_{\text{absorption}} \) are properties inherent to the semiconductor photoanode BiVO_4, its charge-separation and charge-transfer efficiencies might both be affected by a catalyst. In the hole-scavenger, with \( \eta_{CT} = 1 \), the photocurrent can be approximated as:

\[
j_{hs} = j_{\text{max}} \cdot \eta_{\text{absorption}} \cdot \eta_{CS}
\]

Therefore, the charge-transfer efficiency \( \eta_{CT} \) can be calculated as:

\[
\eta_{CT} = \frac{j_{\text{H}_2\text{O}}}{j_{hs}}
\]

It is to be noted that the concentration of the hole-scavenger has to be high enough in order to obtain maximum charge transfer. We performed experiments in 1 M and 0.1 M Na_2SO_3 as hole-scavenger (hs), in which the 0.1 M concentrated solution has shown not to be 100 % efficient. Figures S16a and b show the CV scans of bare (S16a) and modified (S16b) BiVO_4 in different hs concentrations. The obtained CV of bare BiVO_4 in 0.1 M hs shows less current density than that obtained in 1 M hs, indicating that it is not 100 % efficient in only 0.1 M concentration. Therefore, 0.1 M Na_2SO_3 cannot be used as a reference for calculating \( \eta_{CT} \) via \( \eta_{CT} = \frac{j_{\text{H}_2\text{O}}}{j_{hs}} \).

**Figure S16**: Cyclic voltammograms (50 mV/s) under light (1sun illumination) of a) bare and b) CoFe-PB coated BiVO_4 in buffer (black), 0.1 M (red) and 1 M (green) Na_2SO_3 containing buffer solution (0.1 M KPi).
Table S4 shows the obtained catalytic efficiencies at distinct potentials for different systems. Different CoFe-PB modified systems did not show any clear trend, they all have similar charge-transfer characteristics. This indicates that CoFe-PB acts as a real charge-transfer catalyst, independent of the coating thickness. The catalytic efficiency of CoOₓ/BiVO₄ is smaller at potentials below 1.4 V vs RHE than most CoFe-PB modified systems, showing a more anodic optimum potential, which, again, indicates superior performance of the CoFe-PB /BiVO₄ photoanodes.

Table S4: Charge-transfer efficiencies and potentials, at which ηₜₐₜₜ is maximal, therefore the optimum operation potentials (vs RHE), for bare BiVO₄ electrodes, CoFe-PB/BiVO₄ systems with varying catalyst thickness and CoOₓ/BiVO₄.

| System         | Optimum Potential | ηₜₐₜₜ | ηₜₐₜₜ | ηₜₐₜₜ | ηₜₐₜₜ | ηₜₐₜₜ |
|----------------|-------------------|-------|-------|-------|-------|-------|
| bare BiVO₄     | 1.6 V *            | 0.02  | 0.05  | 0.09  | 0.14  |       |
| x3-CoFe-PB/BiVO₄ | 1.24 V           | 0.48  | 0.74  | 0.84  | 0.66  |       |
| x3-CoFe-PB/BiVO₄ | 1.18 V           | 0.30  | 0.51  | 0.58  | 0.30  |       |
| x4-CoFe-PB/BiVO₄ | 1.17 V           | 0.34  | 0.68  | 0.75  | 0.41  |       |
| x4-CoFe-PB/BiVO₄ | 1.18 V           | 0.42  | 0.68  | 0.73  | 0.41  |       |
| x5-CoFe-PB/BiVO₄ | 1.22 V           | 0.15  | 0.40  | 0.57  | 0.37  |       |
| x6-CoFe-PB/BiVO₄ | 1.18 V           | 0.59  | 0.73  | 0.74  | 0.43  |       |
| CoOₓ/BiVO₄     | 1.4 V             | 0.49  | 0.58  | 0.64  | 0.64  |       |

* bare BiVO₄ electrodes reach highest ηₜₐₜₜ always at the maximum applied potential. i.e. ηₜₐₜₜ increases with Vₐₚₙₙₐₜₑₜ.

10.2. Charge-separation efficiency

From the same experiment in hole scavenger, the charge-separation efficiency ηₚₚₑₚₑₑₑ of the system can also be extracted, because of relation (S10), which gives:

$$\eta_{CS} = \frac{j_{hs}}{j_{max} \eta_{absorption}}$$  \hspace{1cm} (S10)

The maximum absorbed photocurrent \( j_{abs} \) was calculated from the optical measurements (transmittance and reflectance between 300 and 550 nm) by:
\[ j_{\text{abs}} = \frac{e}{h c} \int I_\lambda(1 - 10^{-A}) \, d\lambda \]  

(S11)

with \( I_\lambda \) being the light intensity at a certain wavelength \( \lambda \) and \( A \) being the absorption coefficient.

The obtained 7.25 m/\( \text{cm}^2 \) is close to the theoretical value 7.50 m/\( \text{cm}^2 \) for BiVO\(_4\) and is not influenced by the catalyst, since the catalyst does not contribute to light harvesting as described earlier in the text.

**Figure S17** shows the calculated charge-separation efficiency \( \eta_{CS} \) as a function of applied bias. As higher the applied potential, as better charges separate, thus leading to higher \( \eta_{CS} \). Modification with the catalyst increases the charge separation only by about 5 \%, which supports the assumption that the main role of the CoFe-PB catalyst is not the enhancement of charge separation, but its catalytic activity.

**Figure S17**: Charge-separation efficiency of bare BiVO\(_4\) (black) compared to CoFe-PB coated BiVO\(_4\) (red) calculated from CV in 1M Na\(_2\)SO\(_3\) under 1 sun illumination.
11. EIS

At all potentials, a single arc was obtained in the Nyquist plot (see Figure S18a). Consequently, the data were fitted to a Randles’ equivalent circuit, (see inset in Figure S18a), from which the series resistance (R_s), the charge transfer resistance (R_{ct}) and the capacitance (C) were extracted (see Figure 9 in the main text and Figure S18b). The series resistance mainly depends on the electrical contacts and wiring to the potentiostat and, hence, was not influenced by the catalyst.

**Figure S18**: a) Nyquist plot of complex Z’’(Ω) vs real impedance Z’(Ω) for three distinct voltages. A single arc was obtained for all applied potentials. b) Series resistances in dependence of applied bias for bare (black circles) and different CoFe-PB modified BiVO_4 electrodes, obtained by modeling the electrochemical system to a simple Randles-Circuit with constant phase element.
12. Computational modeling

Pure density functional theory (DFT) calculations are known to overestimate electron delocalization due to the DFT-inherent self-interaction error, while hybrid functionals, which generally include 20-25% exact Fock exchange, often overcorrect the self-interaction error, leading to exaggerated band splittings. Hence, neither traditional hybrids, nor pure DFT, correctly describe the complex electronic and magnetic structure of Prussian blue type solids.\textsuperscript{14}

Additionally, in this computational study we assume an ideal stoichiometric model structure KCo[Fe(CN)\textsubscript{6}], as its main electronic properties are expected to be similar to the real structure.

A modified hybrid functional (HSE03-13), containing 13\% of exact exchange and screening the long range exchange with a screening parameter of $\mu = 0.3$ Å\textsuperscript{-1}, was found to optimally describe the spin-crossover compound KCo[Fe(CN)\textsubscript{6}] (Figure S19).\textsuperscript{15,16} In order to find the appropriate amount of included exact exchange ($V_{EX}$), a screening of $\%V_{EX}$ was carried out, by implementing the HSE03 functional with $\mu = 0.3$ Å\textsuperscript{-1}. For the geometry optimization, a gamma-centered KPOINT grid and a cut-off energy of 500 eV were used and the electronic charge density was inherited from an initial PBEsol calculation. The band gap was chosen as the main fitting criterion for finding the optimal $\%V_{EX}$, as demonstrated in Figure S19. Other electronic and structural parameters are given in Table S5.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figureS19.png}
\caption{Variation of band gap with introduced amount of exact exchange $V_{EX}$ from Hartree-Fock theory.\textsuperscript{17-19}}
\end{figure}

\textsuperscript{17-19}
Table S5 Main parameters of the ideal KCo(III)[Fe(II)(CN)$_6$] in an $ls$-$ls$ magnetic configuration calculated for the functionals PBEsol (Perdew-Burke-Ernzerhof revised for solids), PBEsol + U (with $U_{\text{eff}} = 3$ eV on Co, 5 eV on Fe) and HSE03 (Heyd-Scuseria-Ernzerhof) with varying amounts of exact exchange energy ($V_{\text{EX}}$). All structures and calculations with different hybrid and GGA functionals for the low lying $ls$-$ls$ and $hs$-$ls$ configurations of CoFe-PB have been uploaded to the ioChem-BD database.

| Functional       | Stabilization energy of $ls$-$ls$-state $E_{\text{hs-ls}} - E_{\text{ls-ls}}$, eV | Band gap $AE_g$, eV | Crystal field splitting energy of Co CFSE$_{\text{Co}}$, eV | Crystal field splitting energy of Fe CFSE$_{\text{Fe}}$, eV | Lattice constant $a$, Å |
|------------------|---------------------------------|----------------|------------------|------------------|------------------|
| PBEsol           | 1.91                            | 1.29           | 2.37             | 4.18             | 9.745            |
| PBEsol + U       | 1.82                            | 2.23           | 3.63             | 4.68             | 9.834            |
| $0 \% V_{\text{EX}}$ (HSE03) | 0.88                            | 1.17           | 2.34             | 4.16             | 9.862            |
| $10 \% V_{\text{EX}}$ (HSE03) | 0.84                            | 1.96           | 3.49             | 5.02             | 9.853            |
| $13 \% V_{\text{EX}}$ (HSE03) | 0.77                            | 2.21           | 3.86             | 5.24             | 9.852            |
| $15 \% V_{\text{EX}}$ (HSE03) | 0.69                            | 2.38           | 4.09             | 5.44             | 9.852            |
| $20 \% V_{\text{EX}}$ (HSE03) | 0.49                            | 2.81           | 4.71             | 5.89             | 9.851            |
| $25 \% V_{\text{EX}}$ (HSE03) | 0.27                            | 3.24           | 5.32             | 6.37             | 9.855            |
| Experimental     | -                               | 2.25$^{20,21}$ | -                | -                | 9.96(6)$^{22,23}$ |

It has to be noted that KCo[Fe(CN)$_6$] can adopt two low-lying magnetic minima, the diamagnetic $ls$-$ls$ CoFe-PB, containing $ls$ Co(III) and $ls$ Fe(II), with both metals in $t_{2g}^6$ configuration, and ferri-magnetic $hs$-$ls$ CoFe PB with $hs$ Co(II) in $t_{2g}^5eg^2$ configuration.
and $ls$ $Fe(III)$ in $t_{2g}^5$ configuration. In a completely ordered $fcc$ crystal (as in Figure S20b) at zero K, $lsls$ CoFe-PB is stabilized over $hsls$ CoFe PB by 0.77 eV (HSE03-13). Although the degree of stabilization varies with employed functional, the $lsls$ state, however, always remains more stable (see Table S5). This is why for the alignment of the densities of states (DOS), only the non-magnetic $lsls$ configuration is considered. Nevertheless, it has to be kept in mind that the real, non-stoichiometric CoFe-PB solid at room temperature contains a mixture of magnetic configurations with varying ratios that crucially depend on preparation methods and external factors, such as field, temperature or pressure.

![Theoretical model crystal structures](image)

**Figure S20:** Theoretical model crystal structures of a) monoclinic scheelite $ms$-BiVO$_4$ and b) stoichiometric CoFe-Prussian blue $fcc$ KCo[Fe(CN)$_6$].

In order to align the DOS of BiVO$_4$ and CoFe-PB, a water molecule was incorporated in the porous CoFe-PB structure and energy levels were aligned taking the O $2s$ band as reference level. The incorporation of a water molecule in the CoFe-PB structure does not alter the electronic structure around the Fermi level as shown in Figure S21.
Figure S21: Density of states of CoFe-PB with (left) and without (right) incorporation of a water molecule in the solid lattice (calculated with PBEsol).

Figure S22 shows the DOS of both compounds, calculated initially with PBEsol. Although giving a smaller bandgap, as expected for pure DFT calculations, the PBEsol calculation shows the same trend in having the Co $t_{2g}$ energy levels of CoFe-PB well above the BiVO$_4$ valence band.
**Figure S22:** Density of states of BiVO₄ (left) and CoFe-PB (right) calculated with the PBEsol functional with the CoFe-PB valence band as zero energy level and aligned along the O 2s band of incorporated water in CoFe-PB.
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