Photocurrent of BiVO₄ is limited by surface recombination, not surface catalysis

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Supporting information



Figure S1. A calculated example of complex photocurrent or IMPS spectrum, illustrating the recombination (upper quadrant) and attenuation (lower quadrant) semicircles. Various properties (e.g. charge transfer rate constant, surface recombination rate constant, cell capacitance) can be obtained based on the multiple points of such spectrum.



Figure S2. Band diagram for **a**) a metal **b**) a semiconductor with Fermi level pinning (metal-like behavior) and **c**) a "normal" semiconductor.



Figure S3. Negative of the natural logarithm of (1-EQE) plotted as a function of the square root of the potential subtracted by the valence band position. The curve follows the Gärtner equation for applied biases above 1 V_{RHE} , which means that the applied potential falls across the space charge region.



Figure S4. High frequency photocurrent intercept plotted semi-logarithmically as a function of the potential for bare (black) and CoPi modified BiVO₄ (red).



Figure S5. Change in open circuit potential (Δ OCP) calculated from OCP measurements in the dark and under illumination with a 457 nm cw Ar ion laser with varying light intensities in 0.5M H₂O₂/0.1M KPi electrolyte. The average of Δ OCP = 24 +/- 2 was calculated from data taken starting at a light intensity of AM 1.5. Inset: OCP measurements to illustrate the change in Δ OCP using the same sample and performed in the same electrolyte.



Figure S6. Change in absorption (ΔA) of **a**) FTO/CoPi, **b**) FTO/BiVO₄/CoPi, **c**) bare FTO and **d**) FTO/BiVO₄ as a function of applied potential measured in-situ by UV-Vis. The bare FTO and FTO/BiVO₄ do not show any changes in the absorption, while a clear change is observed for the CoPi modified samples. The measurements on BiVO₄ were done while illuminating the sample with a 365 nm LED. Since the LED is interfering with the absorption spectra, we eliminated this part from the data shown above. The smaller change in optical absorption (indicated by the color bar) of FTO/BiVO4/CoPi compared to the corresponding change for FTO/CoPi is simply due to ~10× difference in CoPi thickness.



Figure S7. Dark current-voltage (j-V) curves of RuO_x deposited on FTO (red) and bare FTO (black). The RuO_x catalyst shows a large decrease of the overpotential and therefore demonstrates its good catalytic properties.