SUPPORTING INFORMATION – 6 pages

Contactless Measurement of Photovoltage in $BiVO_4$ Photoelectrodes

Sahar Daemi,[a] Anna Kundmann,[a] Kathleen Becker,[a] Peter Cendula,[b] Frank E. Osterloh,*,[a]

[a] Department of Chemistry, University of California, Davis, CA 95616, USA (fosterloh@ucdavis.edu)

[b] Faculty of Electrical Engineering and Information Technology, University of Žilina, Liptovsky Mikulas, 03104, Slovakia

Table S1. Semiconductor and junction information.

Semiconductors	**n-$BiVO_4$**
Band Gap / eV	2.4
Dielectric Constant	68.0 [a]
Thickness / µm	1.4
Conduction Band edge / V vs RHE	0.041
Valence band edge / V vs RHE	2.44
E_F (Flatband potential) / V vs RHE	0.10 [b]

Redox Couples	I_3^-/I^-	SO_4^{2-}/SO_3^{2-}	O_2/H_2O_2	HCF $^{3-/4-}$
E^0 / V vs NHE	0.54	0.17	0.70	0.36
E^0 / V vs RHE (calculated)	0.85 at pH 6.7 (KI_3:KI 5:95)	0.17 at pH 9.6	0.70 at pH 4.2	0.70 at pH 5.6
E_F / V vs RHE (experimental)	0.89	0.17	0.80	0.70
Built-in potential (band bending) / V	0.79	0.07	0.70	0.60
Depletion layer width / nm [c]	11	3	10	9

[a] from Wang et al. [1]

[b] from Kim et al. [2]

[c] calculated from Poisson equation.

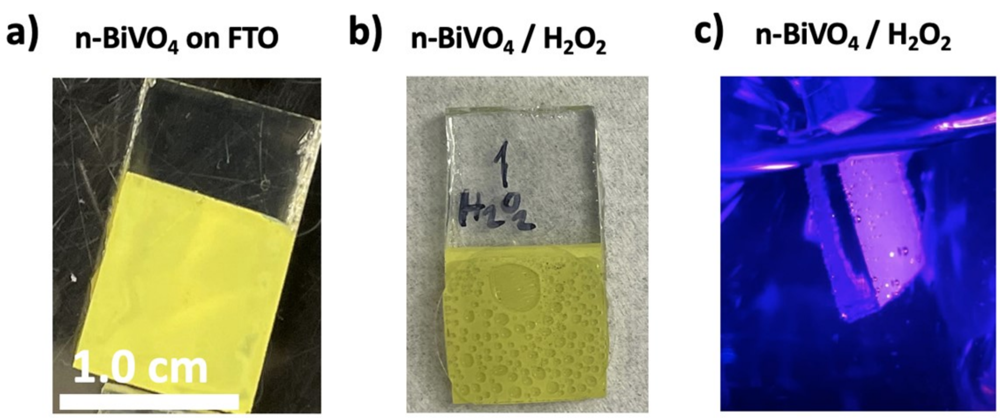

Figure S2. Photos of semiconductor electrodes. a) $BiVO_4$ on FTO. b) $BiVO_4/H_2O_2$ after SPV experiment, c) $BiVO_4$ electrode during short circuit current experiment in aqueous H_2O_2.

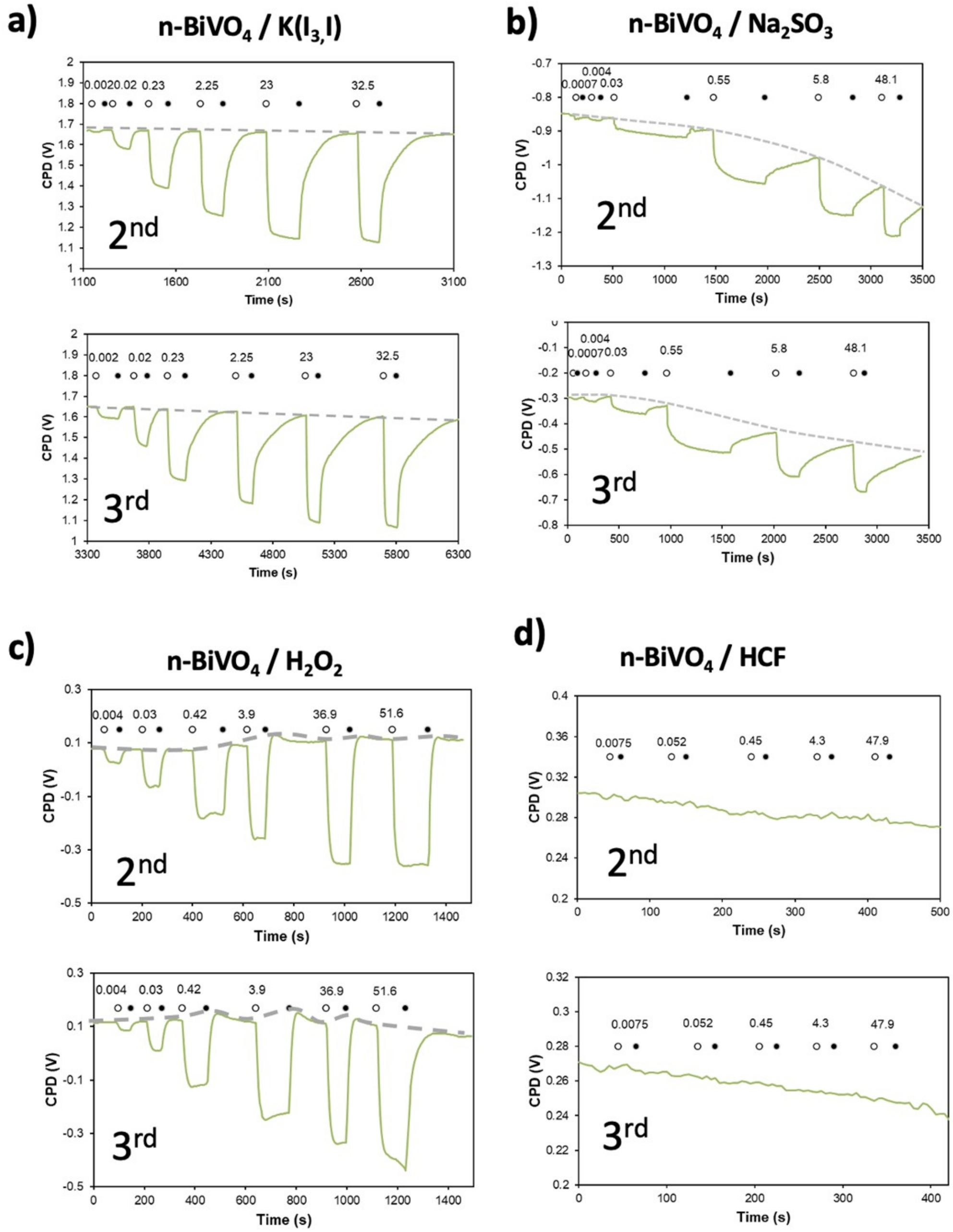

Figure S3. Additional surface photovoltage data under monochromatic illumination of variable irradiance. $BiVO_4$ film on FTO in contact with aqueous solutions of a) KI/KI_3 (470 nm) b) Na_2SO_3 (400 nm), c) H_2O_2 (400 nm), or d) $K_{3/4}[Fe(CN)_6]$ (HCF) (400 nm). Empty circles are light and filled circles are dark periods.

Table S4. SPV statistics. Data from **Figures 3** and **S2**.

$BiVO_4$/ $K(I_3,I)$					**$BiVO_4$/ Na_2SO_3**			
Intensity / mW cm^{-2}	average ΔCPD / V	STD / V	STD / %		Intensity / mW cm^{-2}	ΔCPD / V	STD / V	STD / %
0.002	-0.03	0.02	66		0.0007	-0.012	0.006	50
0.02	-0.15	0.06	37		0.004	-0.03	0.02	67
0.23	-0.31	0.03	9		0.03	-0.075	0.01	13
2.25	-0.42	0.02	4		0.55	-0.158	0.02	13
23.0	-0.50	0.01	2		5.8	-0.167	0.006	4
32.5	-0.52	0.01	2		48.1	-0.17	0.01	6
$BiVO_4$/H_2O_2					**$BiVO_4$/ HCF**			
Intensity / mW cm^{-2}	average ΔCPD / V	STD / V	STD / %		Intensity / mW cm^{-2}	ΔCPD / V	STD / V	STD / %
0.004	-0.035	0.01	28		0.0007	0	-	-
0.03	-0.11	0.02	18		0.004	0	-	-
0.42	-0.24	0.01	4		0.03	0	-	-
3.9	-0.36	0.02	5		0.55	0	-	-
36.9	-0.46	0.02	4		5.8	0	-	-
51.6	-0.49	0.01	2		48.1	0	-	-

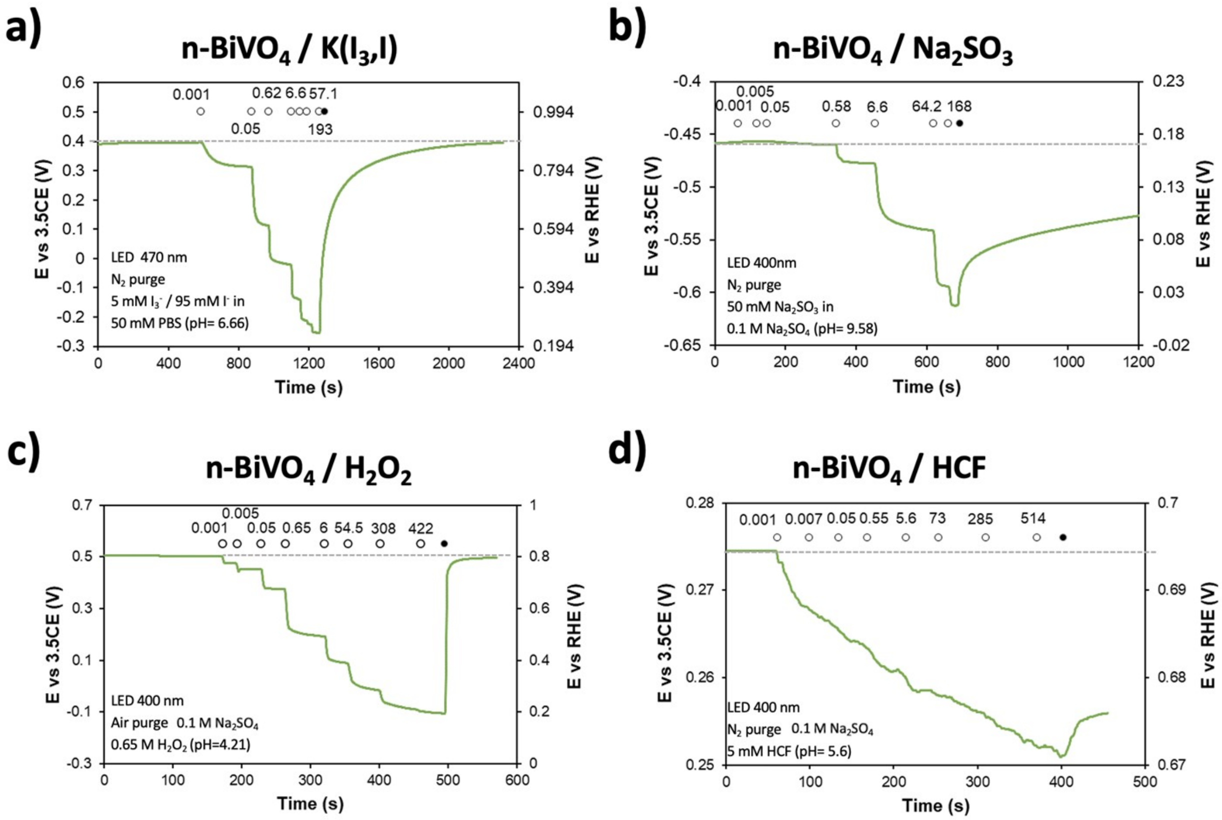

Figure S5. FTO/$BiVO_4$ Fermi levels from OCP measurements versus calomel electrode in the dark and under monochromatic illumination (irradiances given in mW cm^{-2}). For the $K(I_3,I)$ electrolyte a 470 nm LED was used, while all other systems used a 400 nm LED. All electrolytes (except for c) were de-aerated with N_2 gas, except for c. Data in b) was obtained after exposing the $BiVO_4$ photoelectrode to a light-dark cycle (168 mW cm^{-2} of 400 nm) to establish a stable Fermi level in the dark.

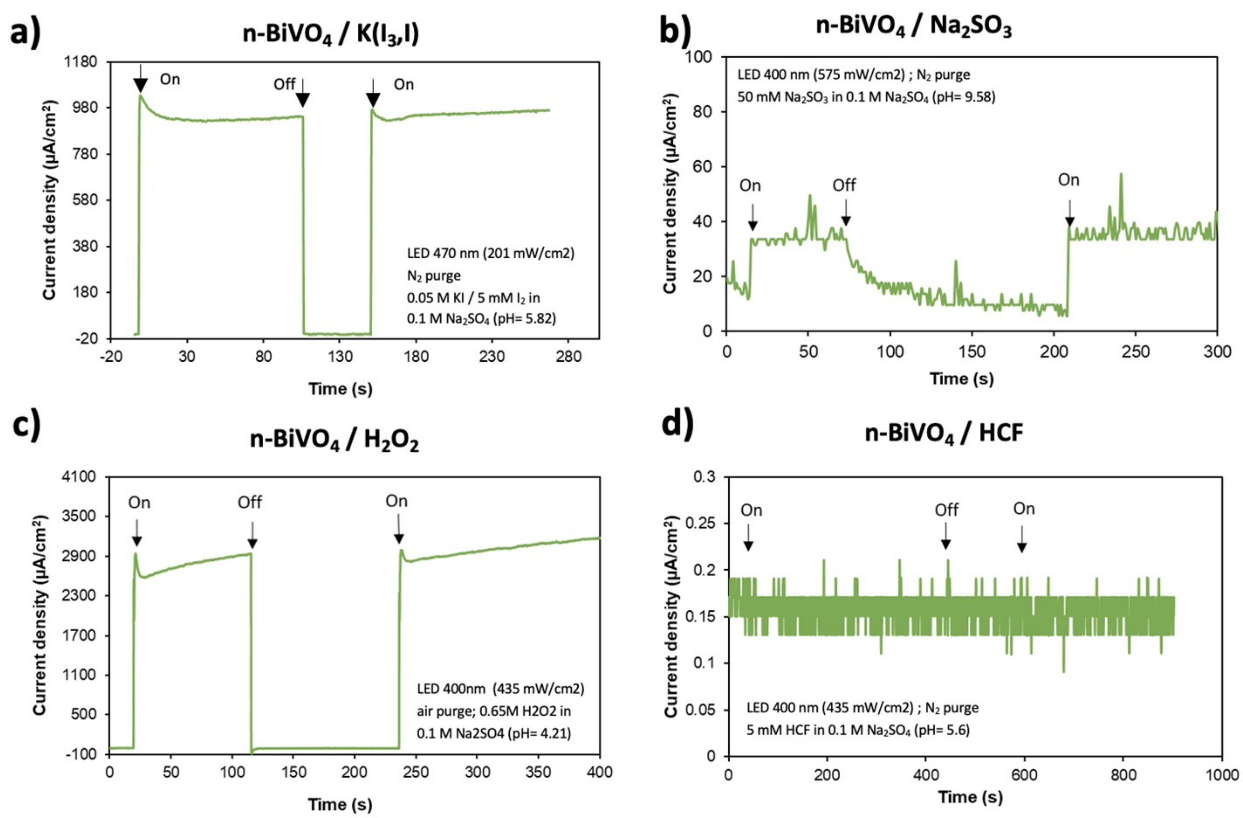

Figure S6. Short circuit photocurrent against Pt counter electrode in aqueous electrolyte. a) n-$BiVO_4$/K(I_3,I) under LED light (470 nm, 201 mW cm^{-2}), b) $BiVO_4$/ Na_2SO_3 under LED light (400 nm, 575 mW cm^{-2}), c) $BiVO_4$/ H_2O_2 under LED light (400 nm, 435 mW cm^{-2}), d) $BiVO_4$/ HCF under LED light (400 nm, 435 mW cm^{-2}). The weak 10 µA cm^{-2} current is attributed to reduction of O_2 traces at the counter electrode. Electrolytes were de-aerated with bubbling N_2 gas, except for c), which was recorded in the presence of air.

References

1. Wang, Q. *et al.* Particulate Photocatalyst Sheets Based on Carbon Conductor Layer for Efficient Z-Scheme Pure-Water Splitting at Ambient Pressure. *Journal of the American Chemical Society* **139**, 1675-1683, (2017).
2. Kim, T. W. & Choi, K.-S. Nanoporous BiVO4 Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. *Science* **343**, 990-994, (2014).