Supporting Information

Photoelectrochemical conversion of glycerol aqueous solution to value-added chemicals using $Bi_2Fe_4O_9$ as photoanode

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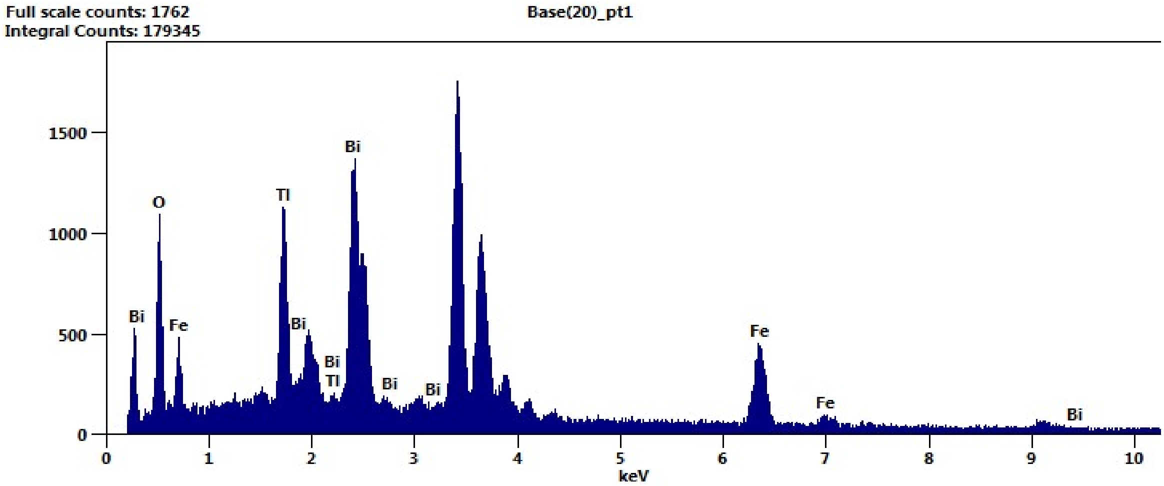
Structural measurements:

From EDX spectra is possible to identify the elements of bismuth ferrite: bismuth, iron and oxygen. The other peaks observed are related to the glass/FTO substrate. The spectra were collected in three different regions of the sample.

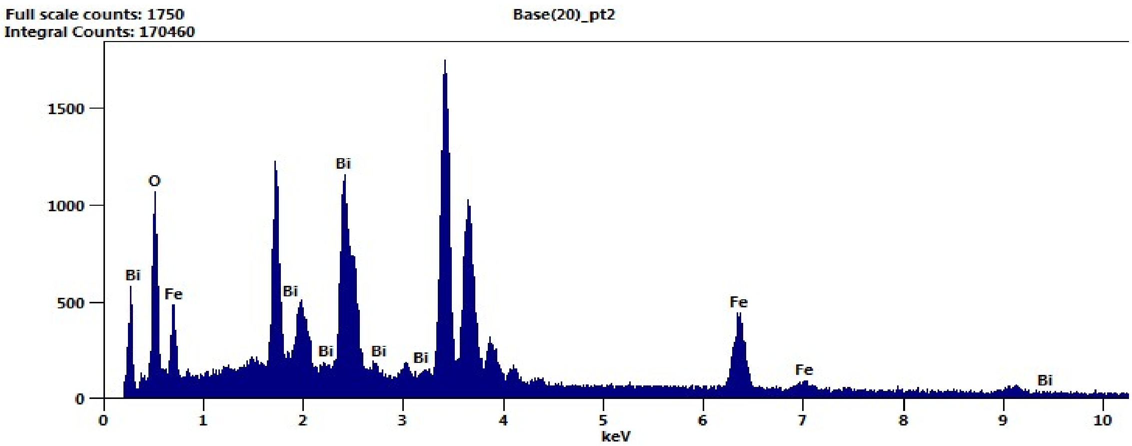
Table S1. Atomic and weight percentage of $Bi_2Fe_4O_9$ in three different areas

	O		***Fe***		***Bi***	
	Atomic (%)	***Weight (%)***	***Atomic (%)***	***Weight (%)***	***Atomic (%)***	***Weight (%)***
Spectrum 1	75.85	30.10	14.54	20.14	9.49	49.16
Spectrum 2	77.17	33.49	15.14	22.93	7.69	43.58
Spectrum 3	77.12	32.92	14.81	22.07	8.07	45.01

Spectrum 1:



Spectrum 2:



Spectrum 3:

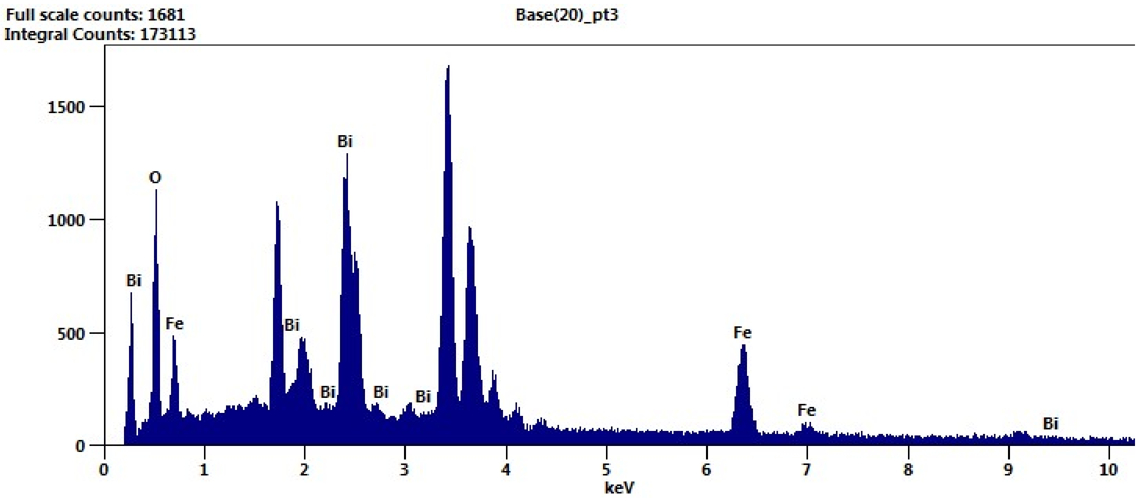


Figure S1. EDX spectra in three different regions of the $Bi_2Fe_4O_9$ photoanode.

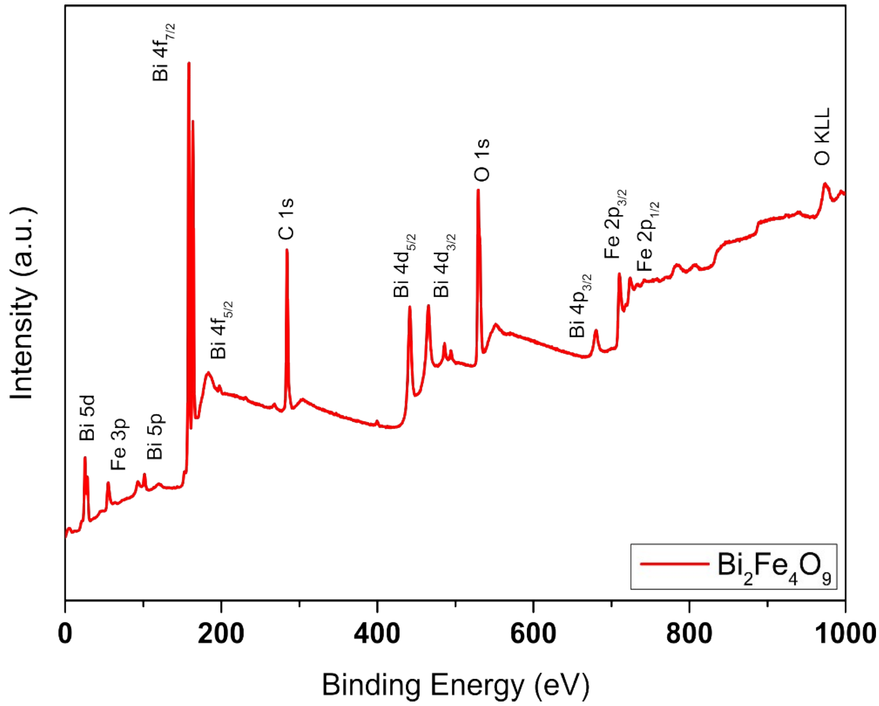


Figure S2. XPS survey spectrum of BFO film

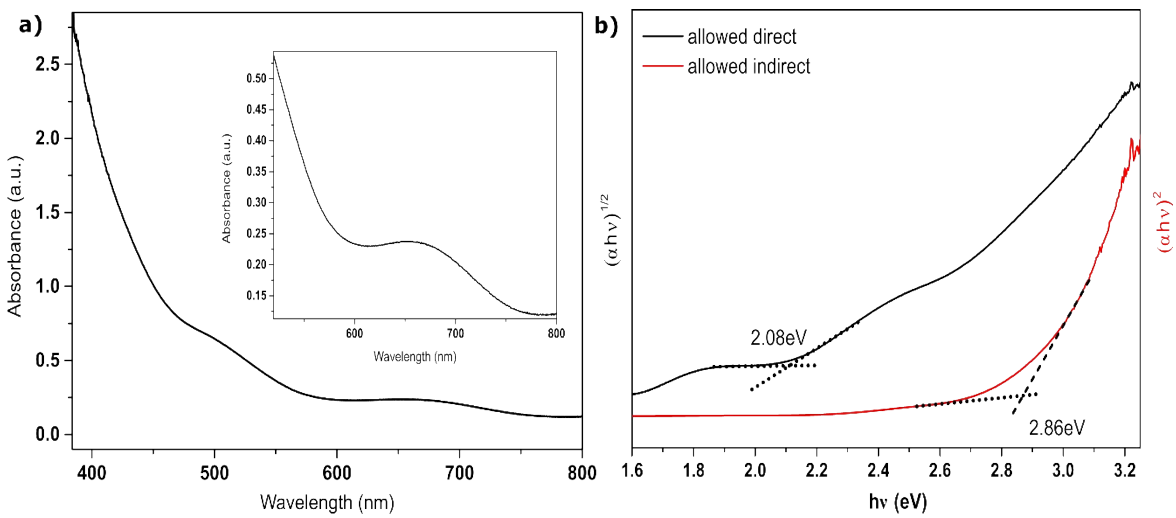


Figure S3. (a) UV-Vis spectra of FTO|BFO and (b) Tauc plots for allowed direct and allowed indirect band gaps indicated in black and red lines, respectively.

Photoelectrochemical characterization:

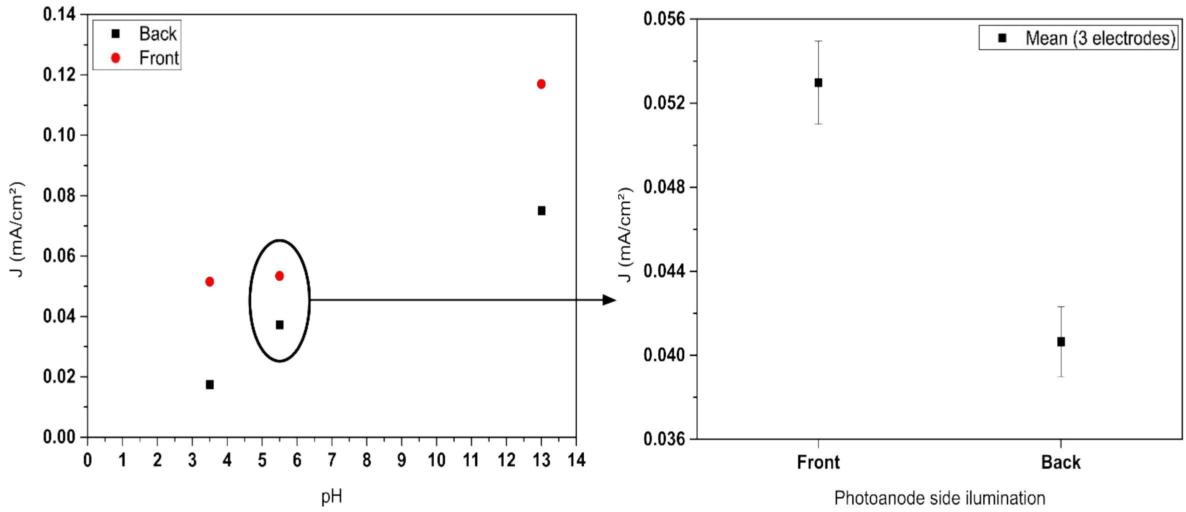


Figure S4. Photocurrent values at 1.23V vs RHE under front-side and back-side illumination (values taken from LSV. For these measurements we used 0.5M Na_2SO_4 as supporting electrolyte. WE: FTO|BFO photoelectrode, CE: Pt foil; RE: Ag/AgCl 3M; scan rate: 10mV s^{-1}).

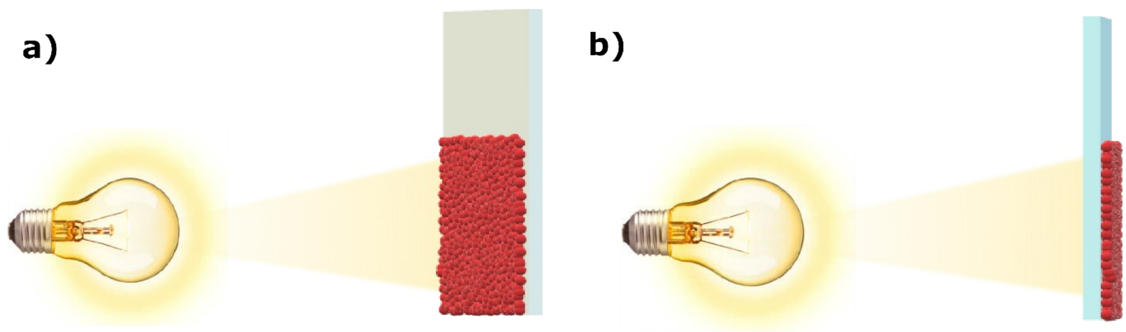


Figure S5. a) Front side illumination and b) back-side illumination.

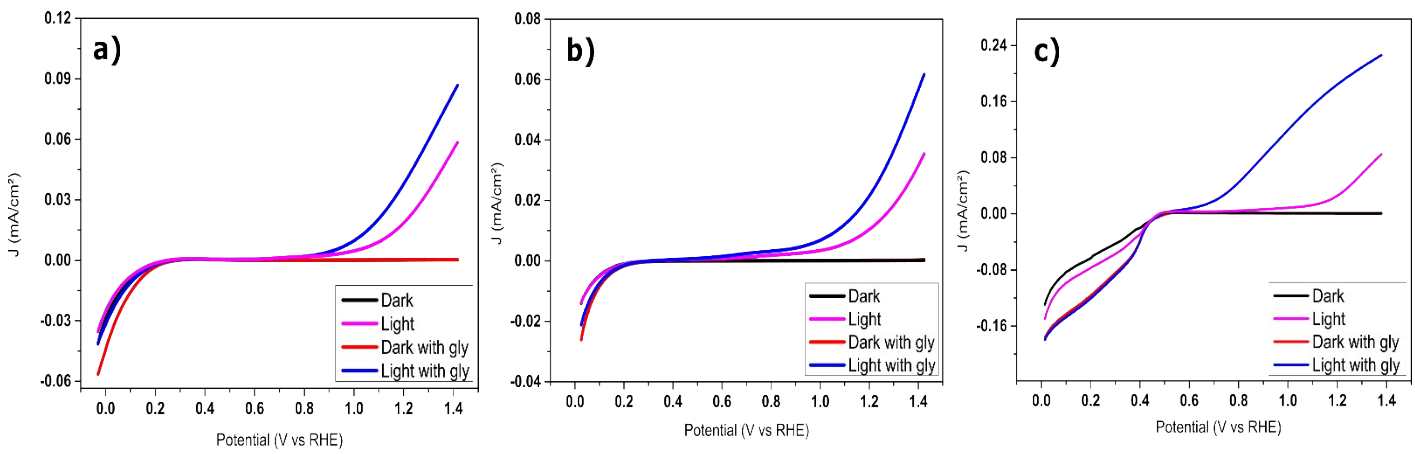


Figure S6. JV profiles of FTO|BFO photoanodes measured in a) 0.3mM H_2SO_4 (pH 3.5) b) 0.2M Na_2SO_4 (pH 5.5) and c) 0.1M NaOH (pH 13) under dark and AM 1.5G illumination conditions.

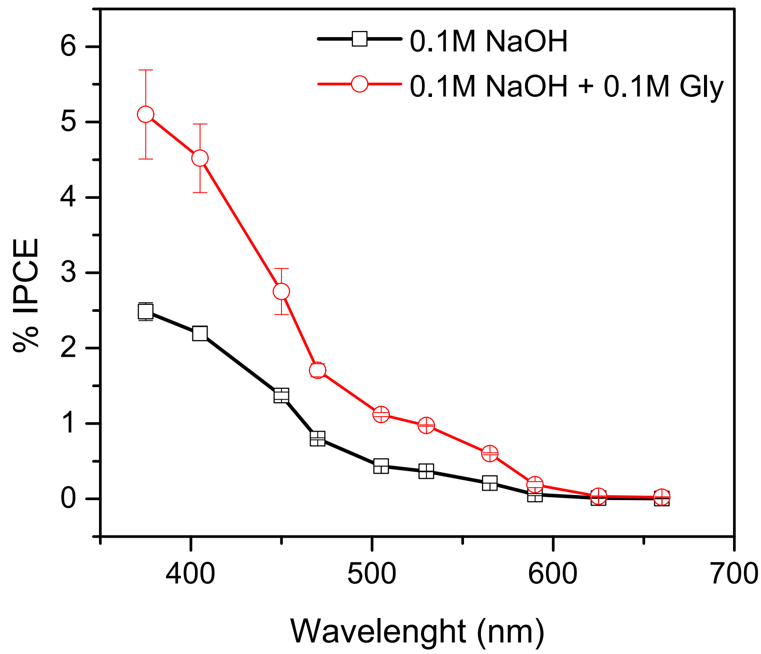


Figure S7. IPCE spectra of FTO|BFO photoanode

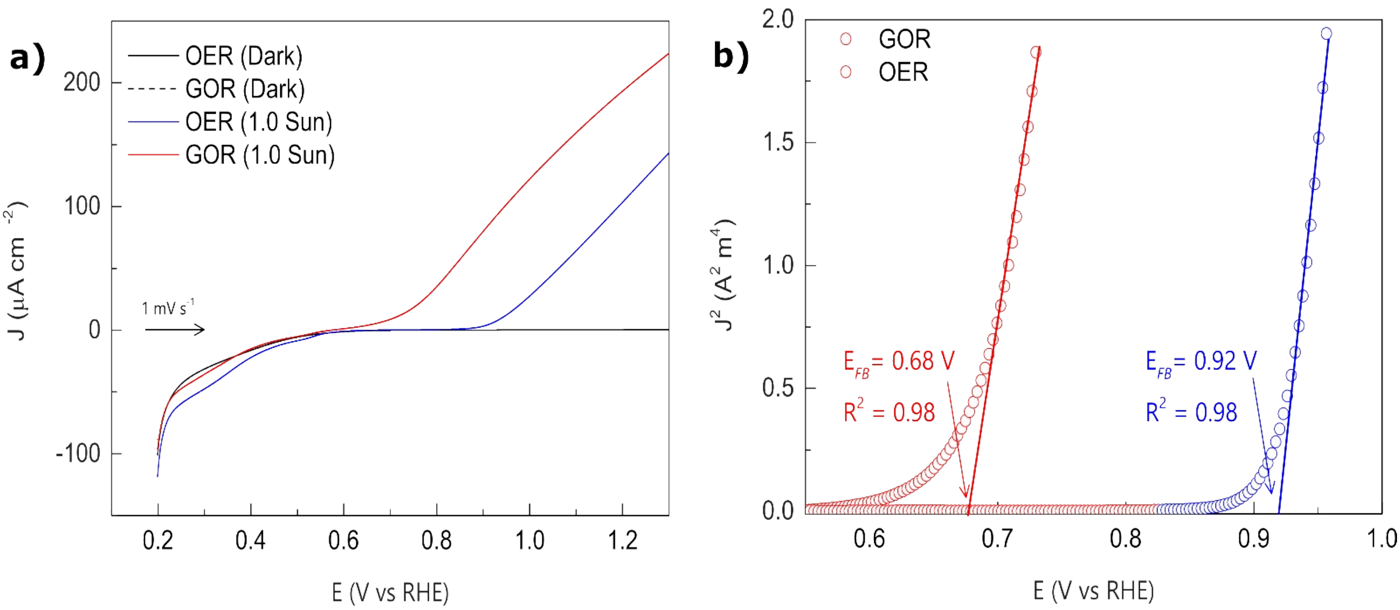


Figure S8. Determination of FTO|BFO flat band. a) LSV at 1.0 mV s^{-1} and b) E_{FB} estimation through Butler-Gartner model

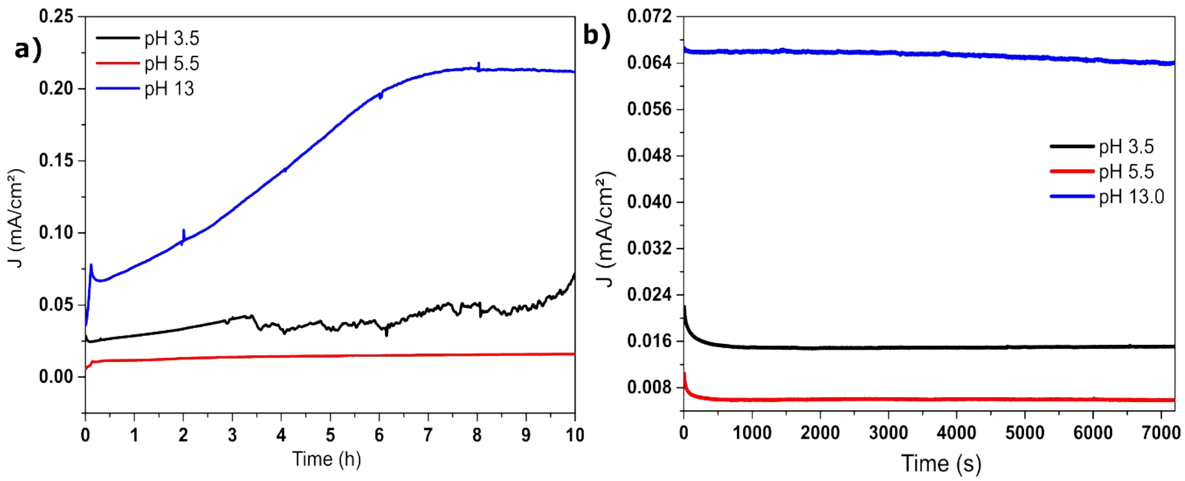


Figure S9. Chronoamperometry at 1.23V vs RHE under AM 1.5G illumination a) with glycerol b) without glycerol.

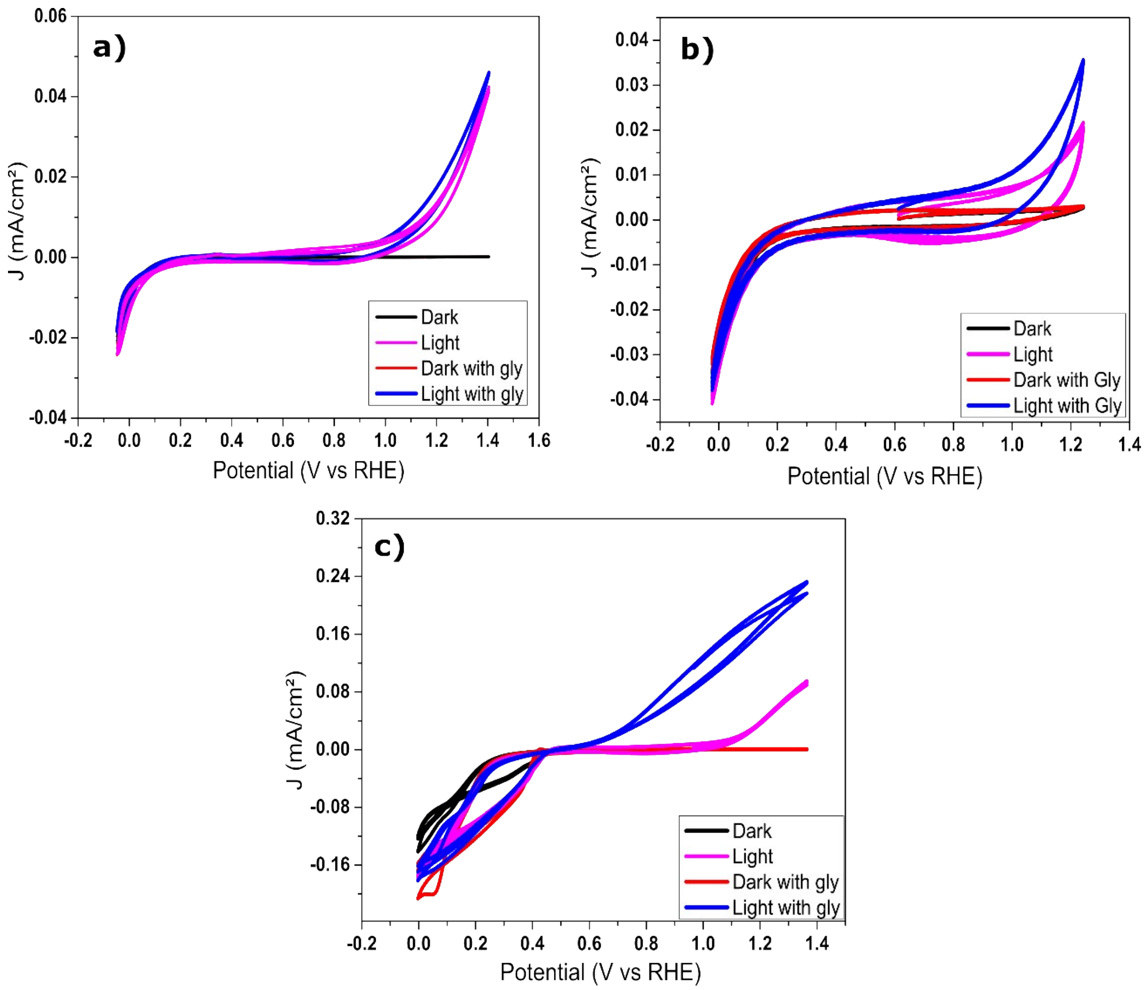


Figure S10. Cyclic voltammograms under dark and light (AM 1.5G) conditions in absence and presence of glycerol at a) pH 3.5 b) pH 5.5 and c) pH 13.0.

OCP Measurements:

After placing the BFO photoelectrode in the electrolyte solution, the Fermi level of this oxide, acquires a constant value (after an initial equilibrium time) due to the chemical species present in the electrolyte. This value corresponds to the open circuit potential in the dark. When the system is illuminated by a light source, the oxide Fermi level shifts upward, occasioning a shift of the OCP toward more negative values (typical behavior of n-type semiconductors), as shown in Figure S8. The difference between the OCP in illuminated conditions and in the dark is called photopotential.[1]

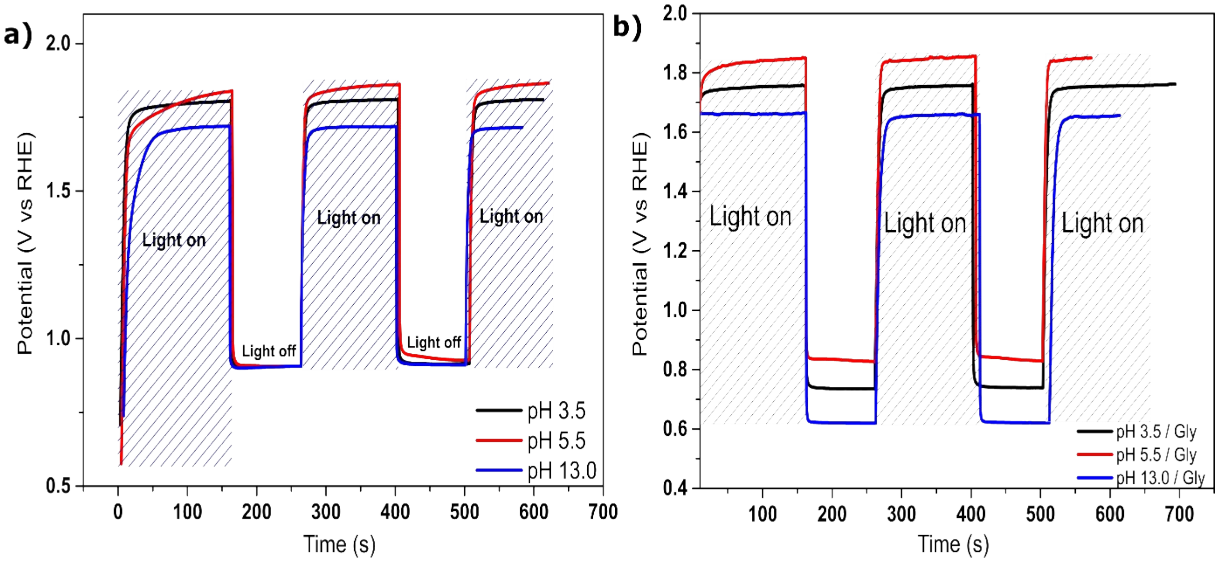


Figure S11. OCP profile under light irradiation and in dark condition. a) absence and b) presence of glycerol.

Once the illumination is interrupted, the relaxation of the OCP was caused solely by the recombination of electron-hole pairs in the photoelectrode. The decay of Voc is proportional to the recombination rate, which lower relaxation values indicate better charge separation. [1] When glycerol was added to the electrolyte, a considerable improvement in the photopotential was observed at pH 3.5 and pH 13 and its values are presented in Table 2.

Table S2. OCP values in dark and light irradiation conditions.

	pH 3.5	**pH 5.5**	**pH 13**	**pH 3.5 with gly**	**pH 5.5 with gly**	**pH 13.0 with gly**
OCP_{dark}	1.82	1.91V	1.72V	1.75V	1.85V	1.66V
OCP_{light}	0.93	0.96V	0.91V	0.73V	0.84V	0.62V
Photopotential	0.89	0.95V	0.81V	1.02V	1.01V	1.04V

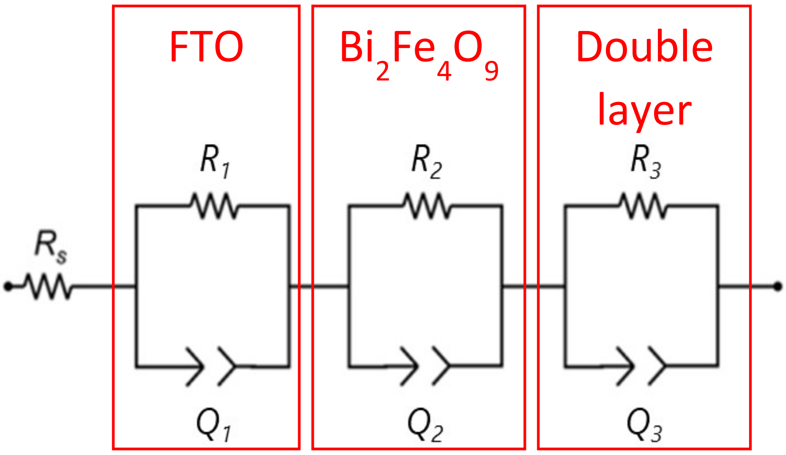


Figure S12. Circuit model used in impedance measurements to obtain resistance and capacitance values.

Table 3. Values of Resistance, capacitance, and χ2 for OER in alkaline medium using FTO|$Bi_2Fe_4O_9$

Eapp	**Rs**	**R1**	**R2**	**R3**	**C1 (eff)**	**C2 (Eff)**	**C3 (eff)**	**χ2**
0.8	124.1	34.3	157	2794	6.47E-06	5.19E-05	3.00E-05	1.40E-05
0.9	12.1	33	655	1684	6.06E-06	2.53E-05	3.80E-05	3.30E-05
1	125.6	32.5	760	1705	5.54E-06	2.34E-05	3.45E-05	5.60E-05
1.1	125.5	31.2	816	1746	5.27E-06	2.38E-05	3.11E-05	7.70E-05
1.2	126	31.2	846	1840	4.83E-06	2.50E-05	2.64E-05	5.90E-05

Table 4. Values of Resistance, capacitance, and χ2 for GOR in alkaline medium using FTO|$Bi_2Fe_4O_9$

Eapp	**Rs**	**R1**	**R2**	**R3**	**C1 (eff)**	**C2 (Eff)**	**C3 (eff)**	**χ2**
0.8	126.9	32.7	160	288000	7.03E-06	4.71E-05	1.42E-04	1.40E-05
0.9	127	33	551	25338	6.54E-06	2.56E-05	1.61E-04	3.30E-05
1	127.1	33.3	645	2975	5.44E-06	2.51E-05	5.47E-05	2.20E-05
1.1	127.8	33	805	2785	5.11E-06	2.22E-05	6.28E-05	6.50E-05
1.2	128.3	31.3	2662	--	4.40E-06	1.48E-05	--	4.00E-05

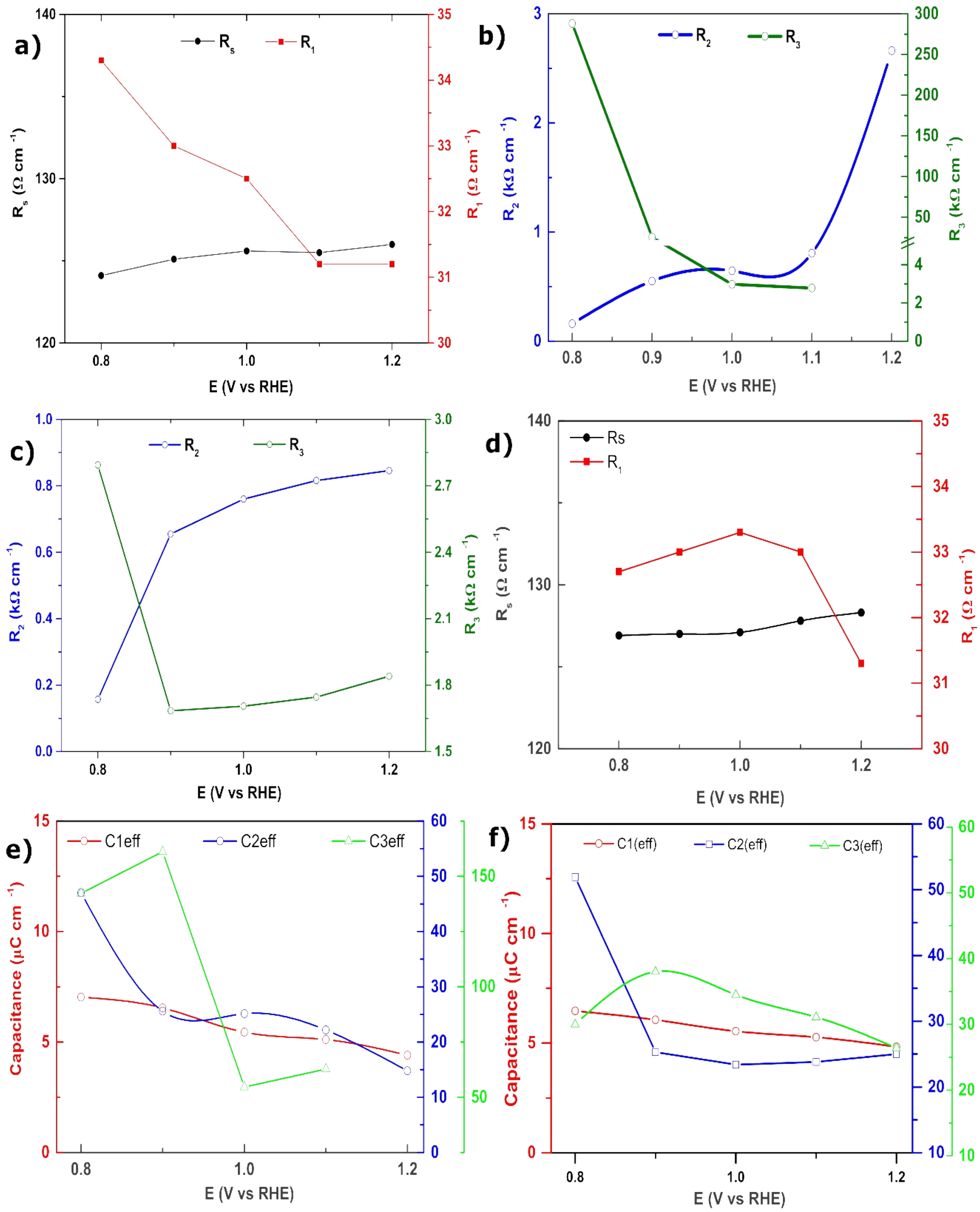


Figure S13. Resistance and capacitance obtained from impedance in alkaline (pH=13.0) medium. a) OER Rs and R_1. b) OER R_2 and R3. c) GOR Rs and R_1 d) GOR R_2 and R_3. e) OER capacitance. f) GOR capacitance.

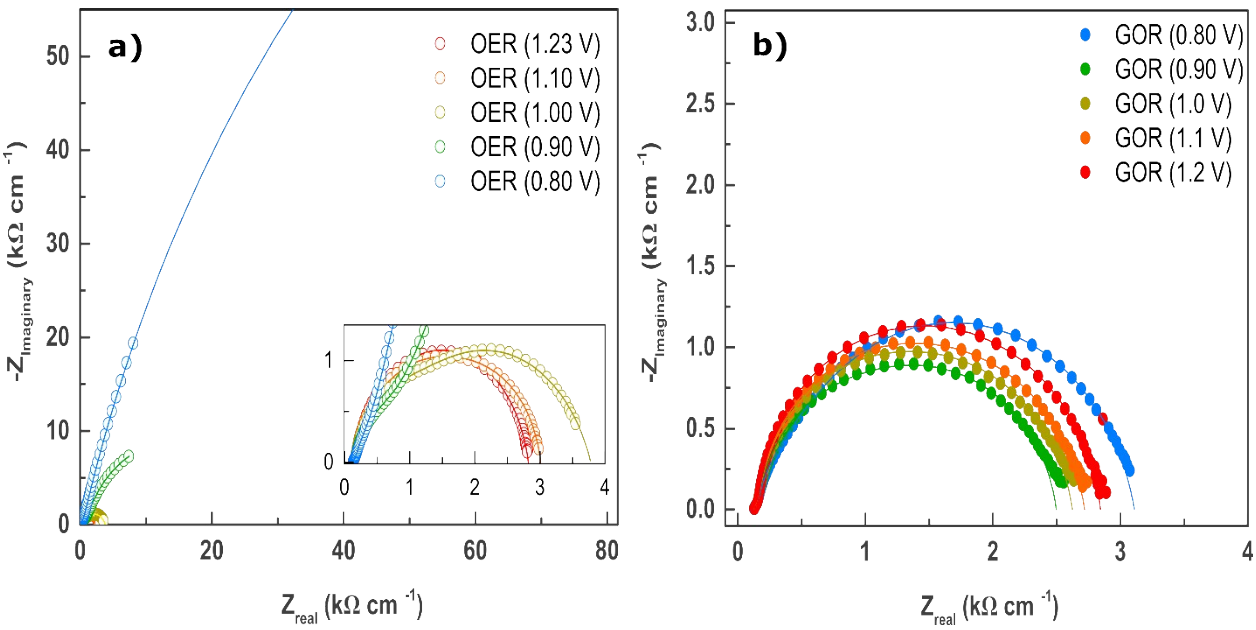


Figure S14 Nyquist Plot measured from 0.8 V to 1.2 V for OER and GOR using FTO|BFO photoanodes in AM1.5 illumination.

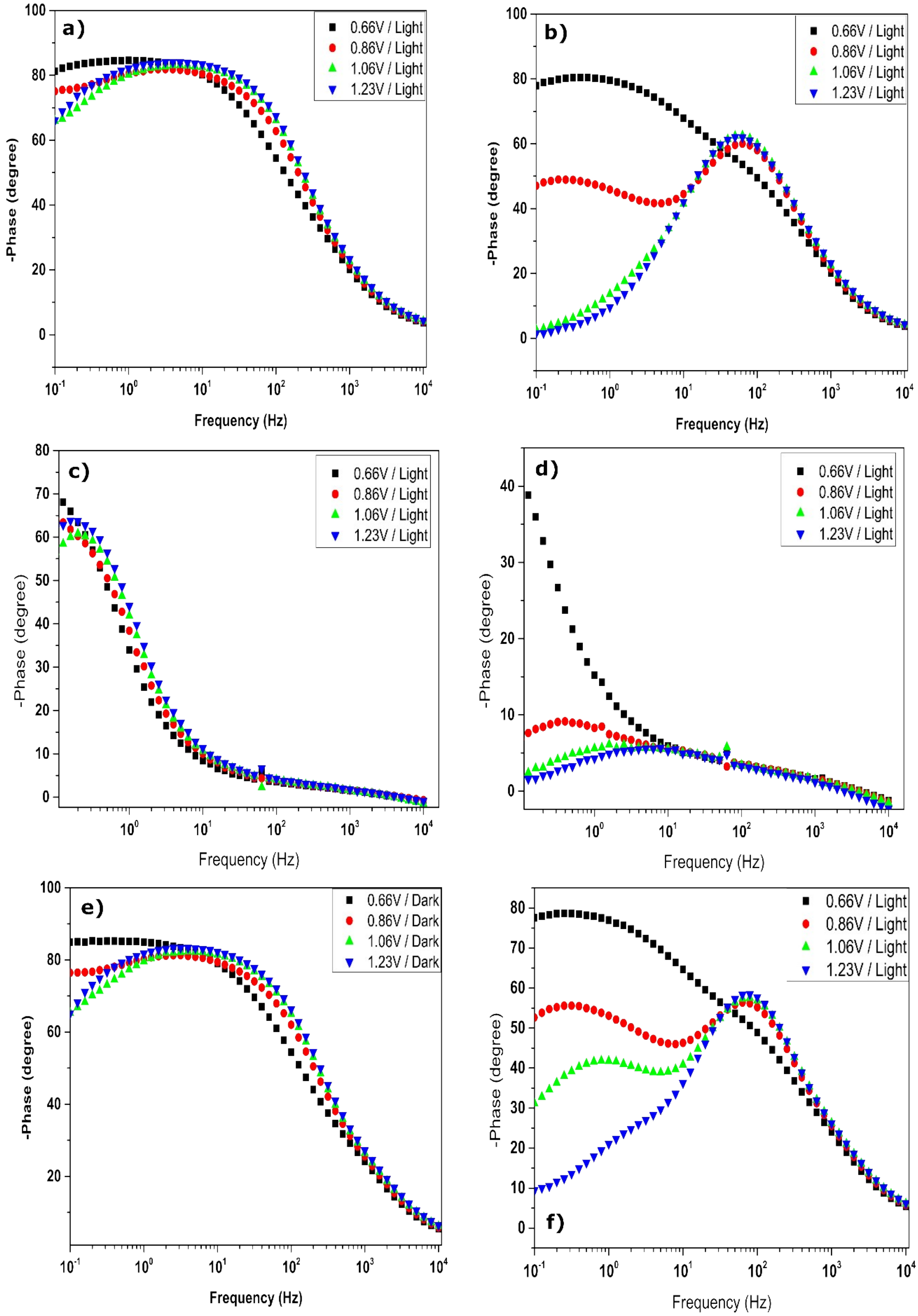


Figure S15. Bode Plots measured at different potentials under dark and AM1.5G condition: a) pH 13.0 Dark b) pH 13.0 Light c) pH 3.5 Dark d) pH 3.5 Light e) pH 5.5 Dark and f) pH 5.5 Light.

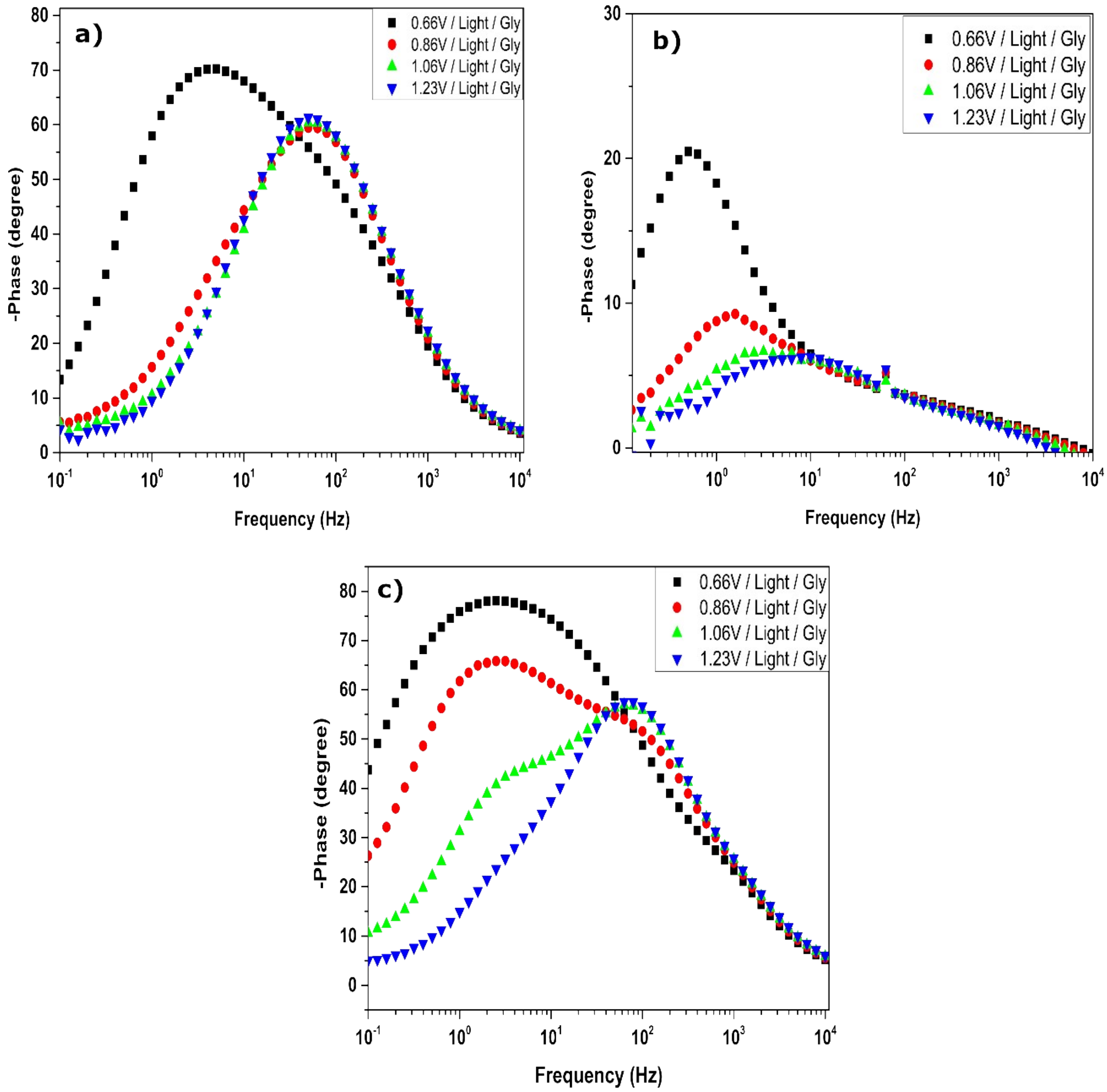


Figure S16. Bode Plots measured under AM1.5G conditions in presence of glycerol. a) pH 13.0 b) pH 3.5 and c) pH 5.5.

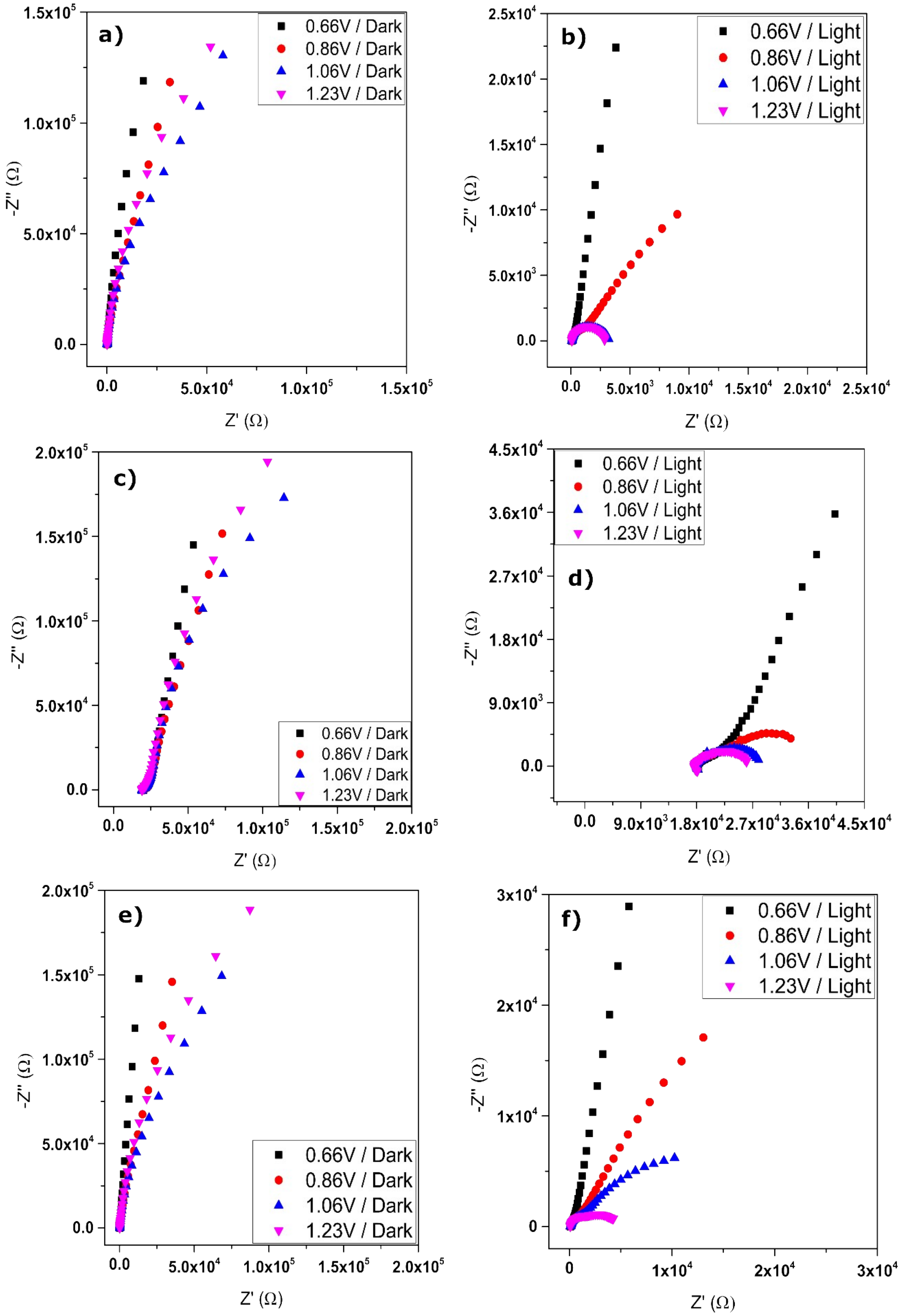


Figure S17. Nyquist Plots measured at different potentials under dark and AM1.5G conditions. a) pH 13.0 Dark b) pH 13 Light c) pH 3.5 Dark d) pH 3.5 Light e) pH 5.5 Dark and f) pH 5.5 Light

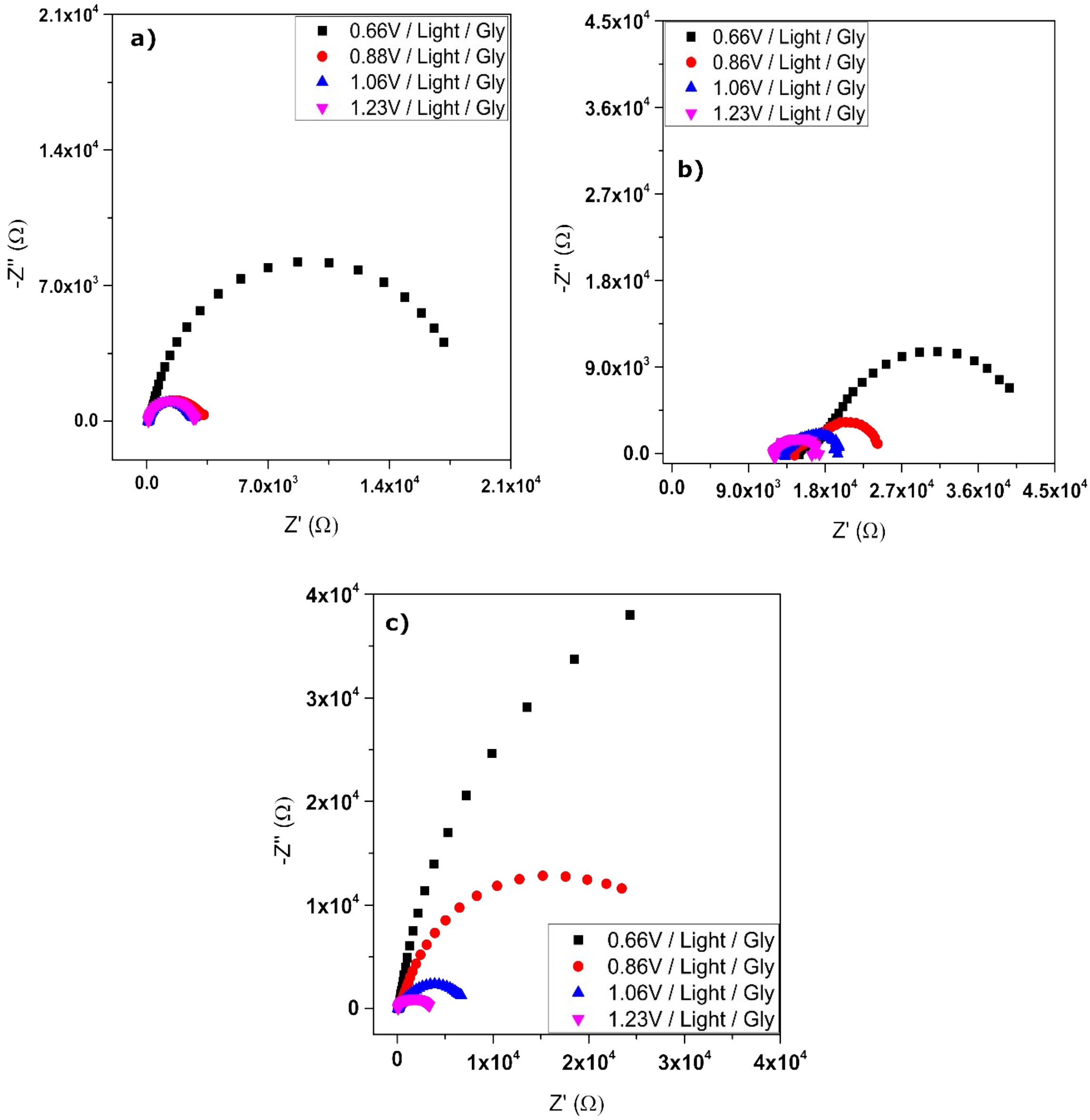


Figure S18. Nyquist Plots measured at different potentials under AM1.5G conditions in presence of glycerol. a) pH 13.0 b) pH 3.5 and c) pH 5.5

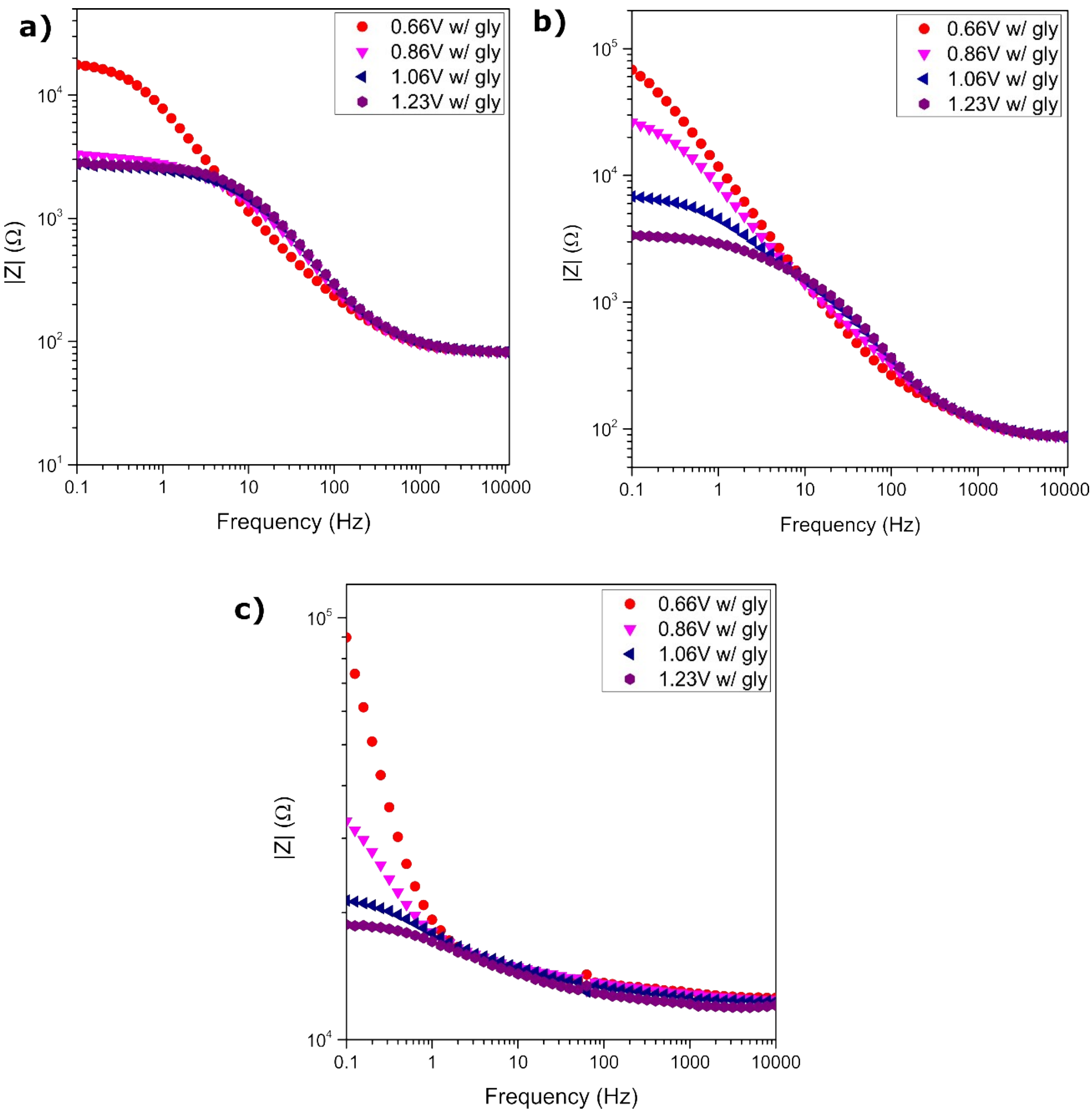


Figure S19. Impedance modulus as a function of frequency for GOR in a) pH 13.0 b) pH 5.5; c) pH 3.5.

Reference

[1] Guijarro, N., Lana-Villarreal, T., & Gómez, R. (2012). Electron Lifetime in Quantum-Dot-Sensitized Photoanodes by Open-Circuit-Potential Measurements. *ChemPhysChem*, *13*(16), 3589-3594.