Effect of Oxygen Evolution Catalysts On Hematite Nanorods For Solar Water Oxidation.

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Experimental:

Materials and method.

All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solutions are prepared using high purity water (resistivity >18 MΩ). F-doped tin oxide was purchased from Solaronix and ultrasonically cleaned for 10 min in soap water, water, acetone, and then isopropanol prior to use.

Synthesis of hematite nanorods

Hematite nanorods were prepared on F:SnO_2 substrates analogous to a procedure described previously.[1] A 15 mL solution containing 0.15 M of $Fe_3Cl_3 \cdot 6H_2O$ and 1M $NaNO_3$ was transferred into a 30 mL scintillation vial and a substrate (2.5 cm x 1.5 cm) was placed at an angle against the wall of the vial with the conducting side facing down. To protect a backside and electrical contact area of the substrate, Kapton tape was applied to the predetermined area before placing the substrate in the vial. A cap was closed tightly and the vial was put in an oven preset to 95 °C. The hydrothermal growth was conducted for 4 hours. The resulting sample was thoroughly washed with deionized water to remove any residual precipitation on the substrate and subsequently sintered in air at 550 °C for 2 hrs to convert FeOOH to hematite film. Further sintering the sample at 800 °C for 15 min resulted in a Sn diffusion doped hematite electrode.

Structural Characterization

Secondary electron microscopy (SEM) images and Energy-dispersive X-ray (EDX) spectra were collected using a JEOL JSM 6700F FE-SEM with an Oxford ISIS x-ray EDS microanalysis system. X-ray diffraction (XRD) analysis was conducted on the samples on F:Sn_2O substrate using Bruker GADDS XRD with two-dimensional (2D) detector. ToF SIMS analysis was performed by CAMECA IONTOF-SIMS IV system with a Bi 25kV analysis gun, at scan area of 150 um by 150 um for 200 scan. XPS measurement were made by VG Escalab 220i XL and the binding energies were calibrated with respect to the residual C (1s) peat at 285.0 eV.

Photodepositon of OECs

A OEC layer were photodeposited as described in a previous report.[2] A hematite electrode was immersed in a Peri dish containing 0.5 mM $Co(NO_3)_2 \cdot 6H_2O$ buffered with 0.1 M potassium phosphate at pH 7 or 1 mM $Ni(NO_3)_2 \cdot 6H_2O$ buffered with 0.1 M potassium borate at pH 9.2. Photodepositon was performed using a hand-held UV light (UVGL-58) with a wavelength of 365 nm with platinum foil short-circuited to the hematite electrode as a counter electrode.

Photoelectrochemical measurements

All PEC measurements were performed in a three-electrode electrochemical cell utilizing a platinum foil as a counter electrode and Ag/AgCl electrode as a reference electrode using an Autolab potentiostat (model PGSTAT30) by Echochimie. A fiber-lite halogen lamp (MI-150, Dolan-Jemmer) was used as a white light source (with 100 mW/cm^2 intensity at the location of the electrode, determined with an OPHIR 3A-SH photodiode). All samples were back-illuminated to avoid nonproductive absorption by the catalyst layer. The hematite substrates were masked with Kapton tape except for a working area of

1.5 cm^2. Electrochemical impedance data were measured with a sinusoidal voltage perturbation of 10 mV amplitude at 1 kHz in dark. Bulk electrolysis was performed in a septum sealed electrochemical cell similar to the PEC measurements but with stirring. The oxygen concentration was measured with a Clark oxygen electrode (Rank Brothers Ltd., Digital Model 10) at the end of the electrolysis.

Fig. S1. XRD spectra collected for hematite nanorods sintered at 800 °C. The solid and dashed lines showed the diffraction peaks of hematite (JCPD 33-0664) and SnO_2 (JCPDS 46-1088), respectively. * denotes SnO_2.

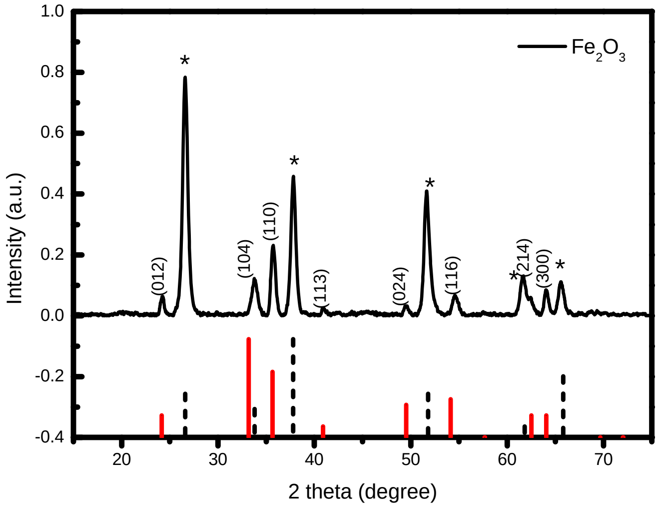


Fig S2. Linear Sweep Voltammograms of (a) Co-Pi/Fe_2O_3 and (b) Ni-Bi/Fe_2O_3 photoanodes in the dark measured in 1 M NaOH electrolyte (pH 13.6) with a scan rate of 50 mV/s.

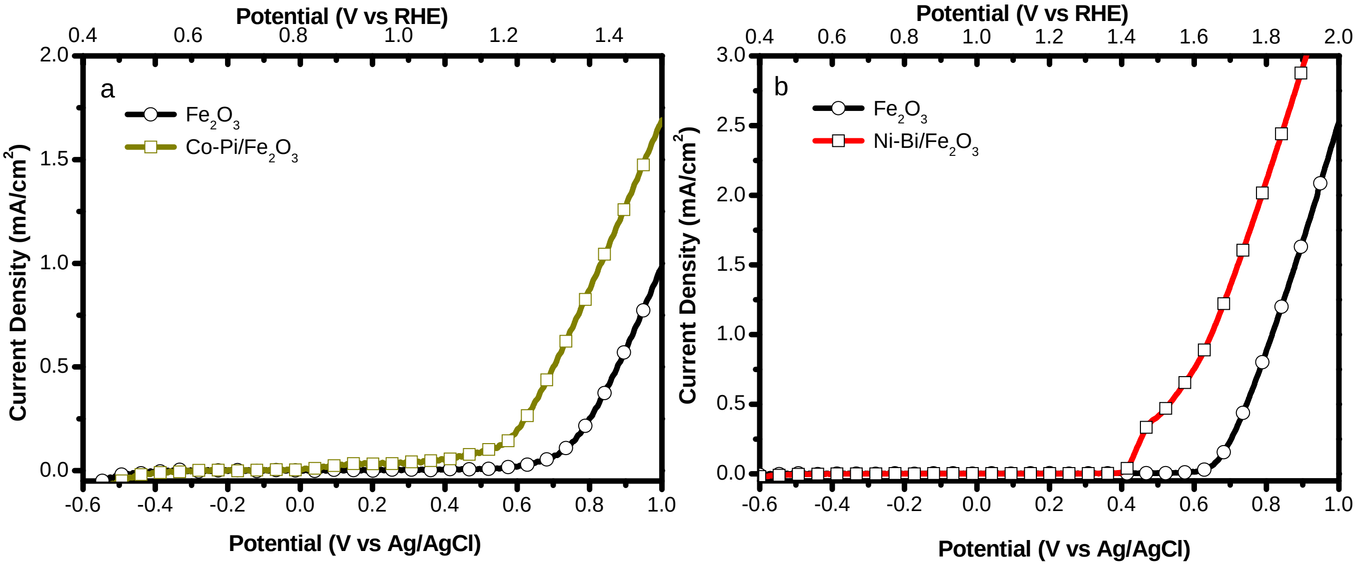


Fig. S3. SEM images of (a) Co-Pi/Fe_2O_3 (b) Ni-Bi/Fe_2O_3 electrode surface.

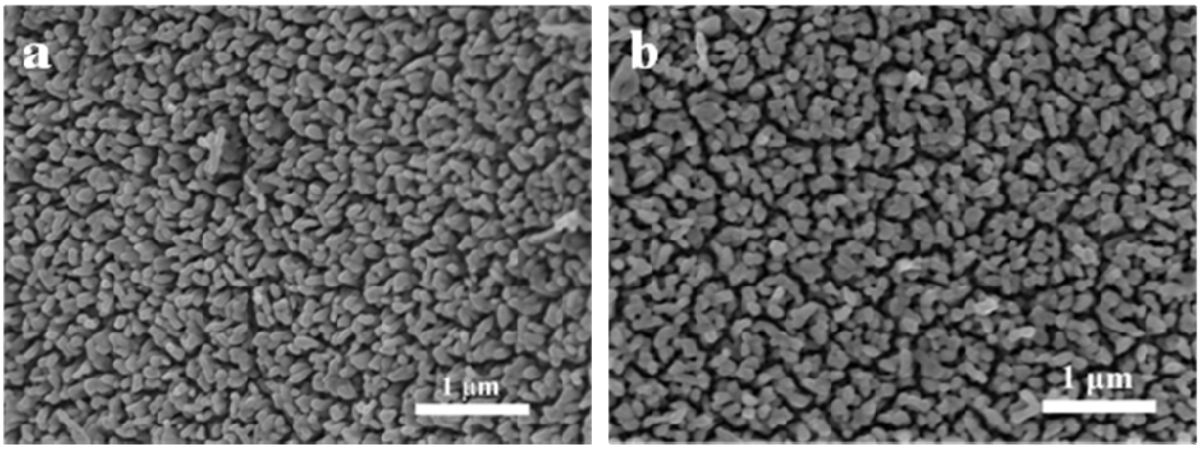
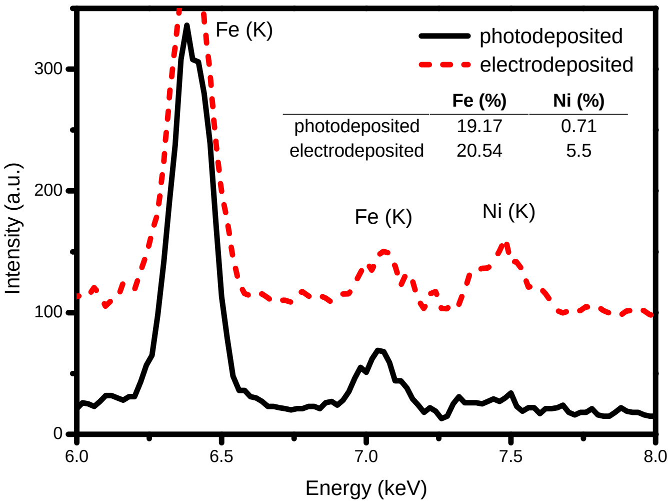
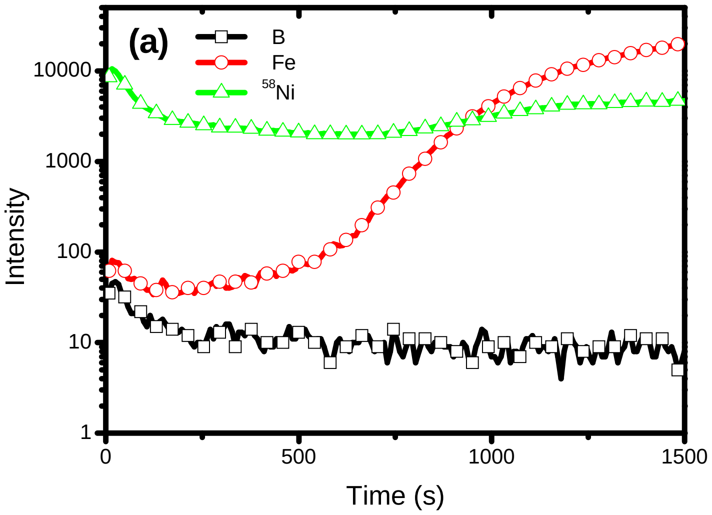


Fig. S4. EDX spectra of a Ni-Bi OEC modified hematite nanorod electrode measured a probe beam of 10 keV. Although a low percentage of nickel was detected, a Ni (K) peak was clearly seen and the amount of nickel detected is comparable to that in the Co–Pi/ Fe2O3 electrode reported previously. This result indicates that a very thin layer of a Ni–Pi OEC covers the surface of the optimized hematite electrode as in the Co–Pi/Fe2O3 composite electrode.[3]



	Fe (%)	Ni (%)
photodeposited	19.17	0.71
electrodeposited	20.54	5.5

Fig. S5. TOF-SIMS depth profiles (a) and special images (b) of a NiBi/Fe_2O_3 electrode. Traces of Ni and B are detected near the surface of the electrode.



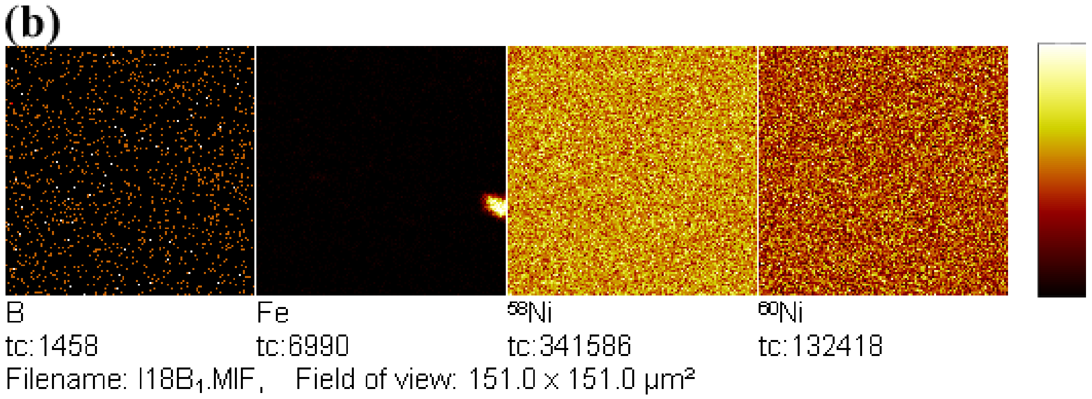


Fig. S6. XPS spectra of the Ni-Bi/Fe_2O_3 film.

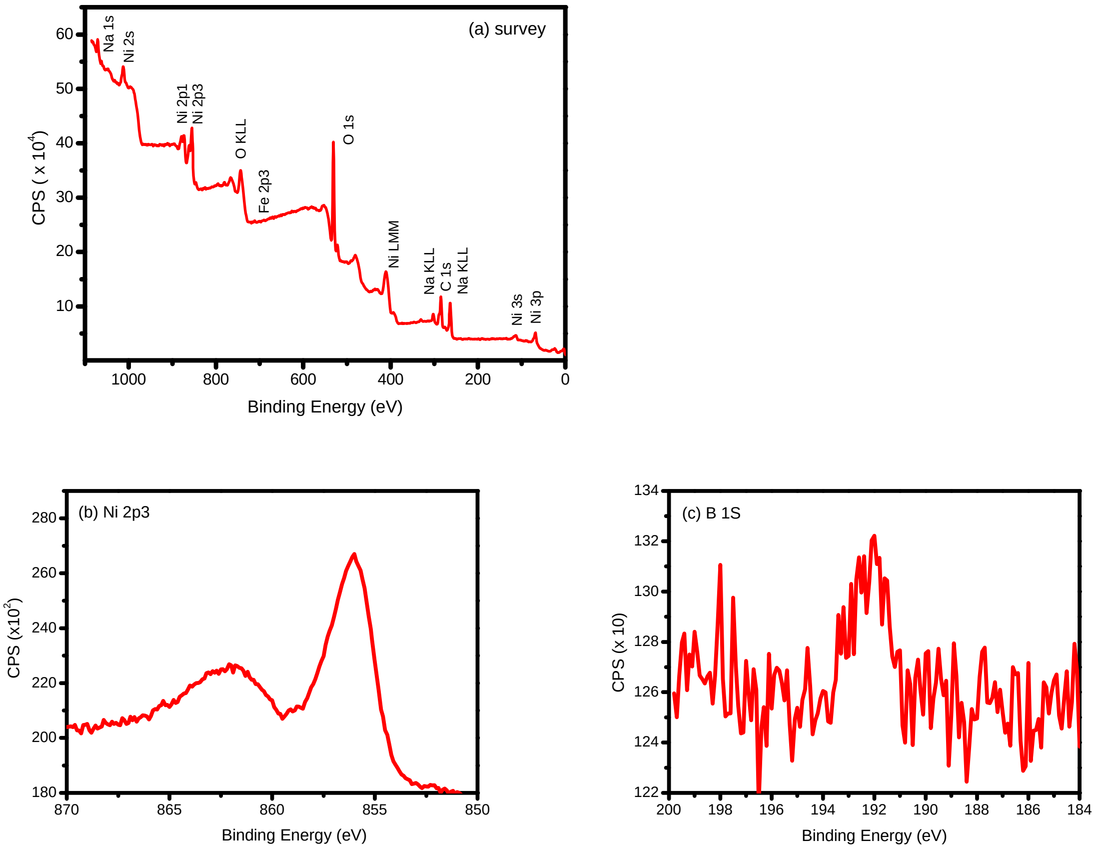


Fig. S7. Photocurrent profile of a bare Fe_2O_3 and a Ni-Bi/Fe_2O_3 electrode under white light illumination (100 mW/cm^2) measured in 1 M NaOH electrolyte (pH 13.6).

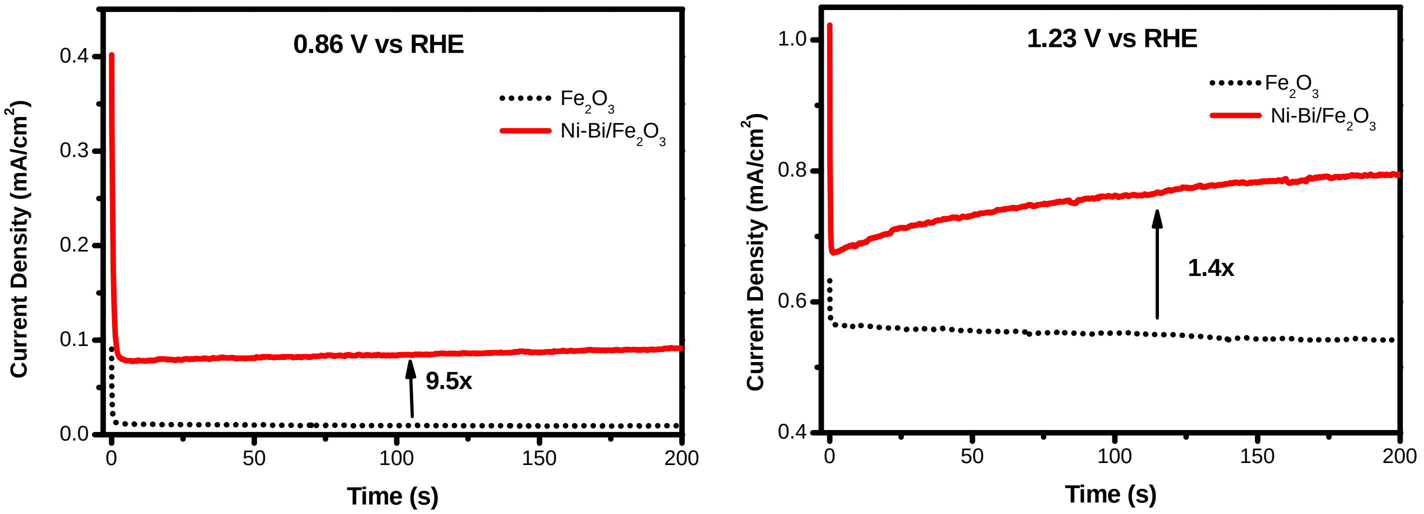
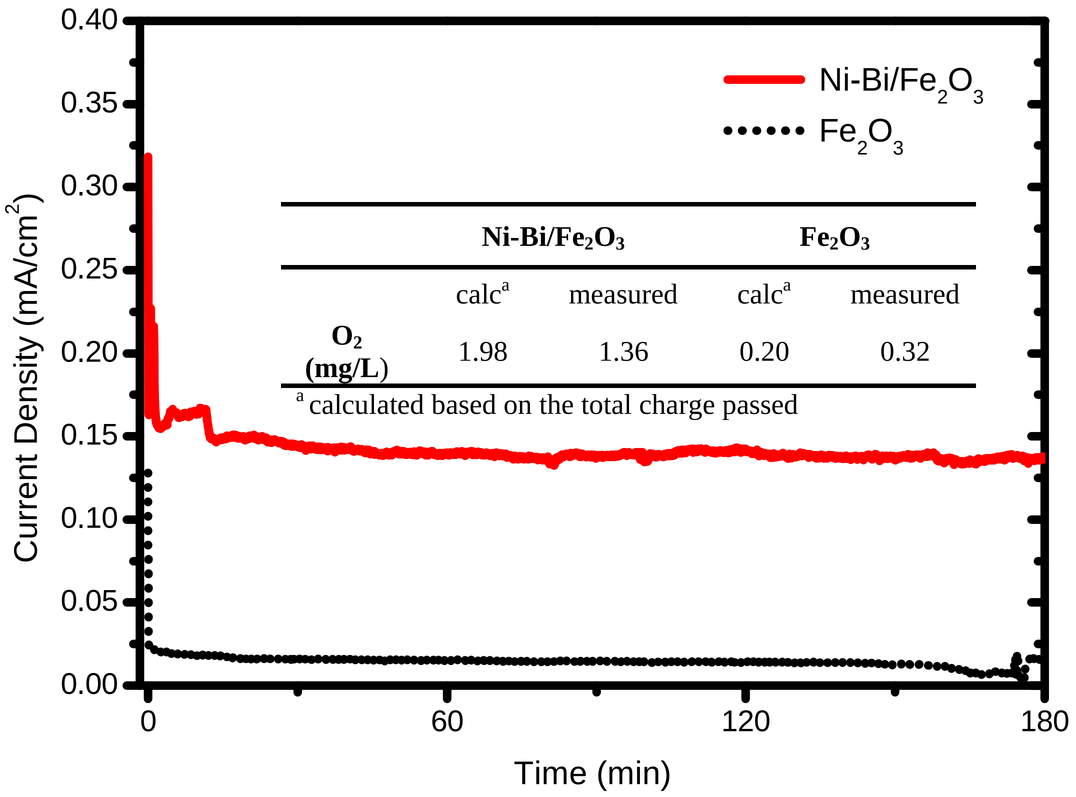


Fig. S8. Photocurrent density profile for a long-term electrolysis at 0.86 V vs RHE under white light illumination (100 mW/cm^2) in 1 M NaOH electrolyte (pH 13.6). Oxygen evolved was measured with a Clark oxygen electrode (Rank Brothers Ltd., Digital Model 10). The discrepancy between theoretical and measured values originates from the Clark cell measurements, which did not include errors due to imperfection of the apparatus, oxygen consumption by the Clark electrode itself, and losses of oxygen to the argon purged headspace in the Clark electrode setup. Fluctuation of current profile is due to bubble formation and to stirring during the electrolysis.



	Ni-Bi/Fe$_2$O$_3$		**Fe$_2$O$_3$**	
	calc[a]	measured	calc[a]	measured
O$_2$ (mg/L)	1.98	1.36	0.20	0.32

[a] calculated based on the total charge passed

Fig. S9. A SEM image of a Ni-Bi/Fe_2O_3 film after repeated long-term electrolysis (total ca. 15 hrs) at either 0.86 V or 1.23 V vs RHE. Although the film shows the sign of aging, its bulk morphology and photocurrent remained unchanged within experimental errors.

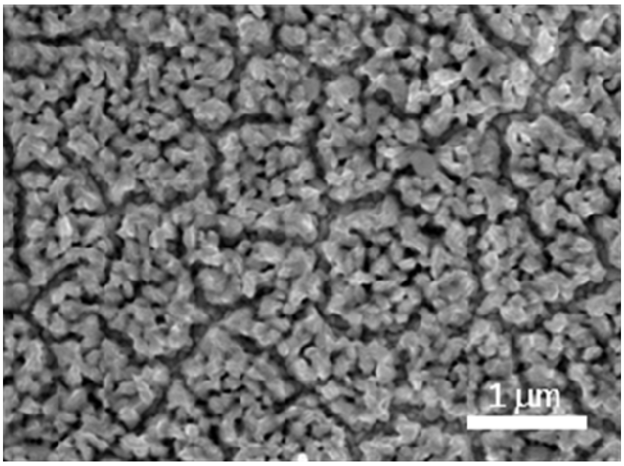
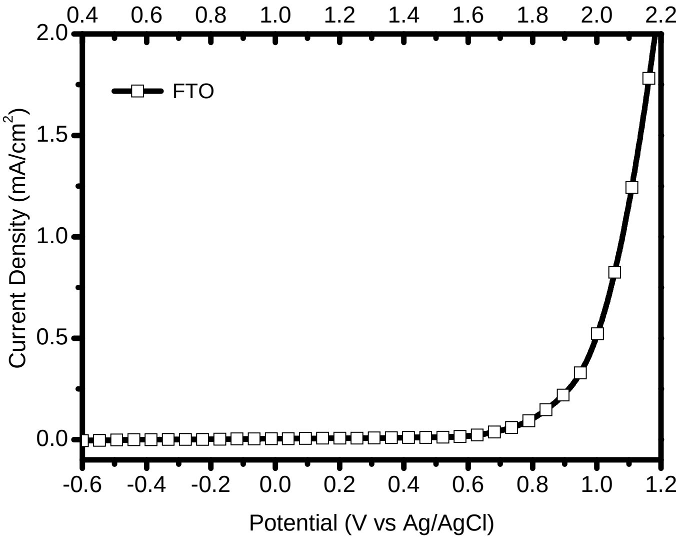


Fig. S10. A Linear Sweep Voltammogram of a base FTO substrate under illumination measured in the same electrolyte after repeated electrolysis with Ni-Bi/Fe_2O_3 photoanodes at various potentials. The possibility that the photocurrent at low potential originates from the solvated Ni^{2+} as a redox mediator can be ruled out due to the failure to detect any electroactive species from the electrolyte after repeated long-term electrolysis.



Reference

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3 D. K. Zhong, M. Cornuz, K. Sivula, M. Graetzel and D. R. Gamelin, Energy Environ. Sci., 2011, 4, 1759.