

## Supplementary Information

### Membrane Inspired Acidically Stable Dye-Sensitized Photocathode for Solar Fuel Production

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#### Supplementary Figures

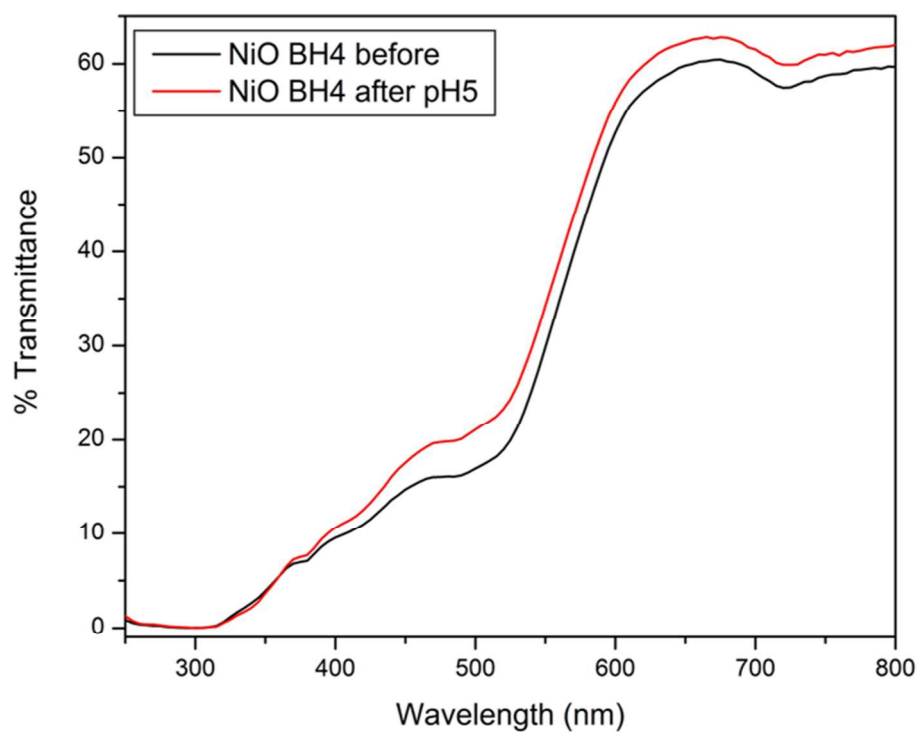


Figure S1. Sensitized BH<sub>4</sub> NiO film before and after 2.7 hours of light chopped chronoamperometry at an applied potential of 0 V vs. NHE in a pH 5 citric acid / citrate buffer with 5mM [Mo<sub>3</sub>S<sub>4</sub>]<sup>4+</sup>

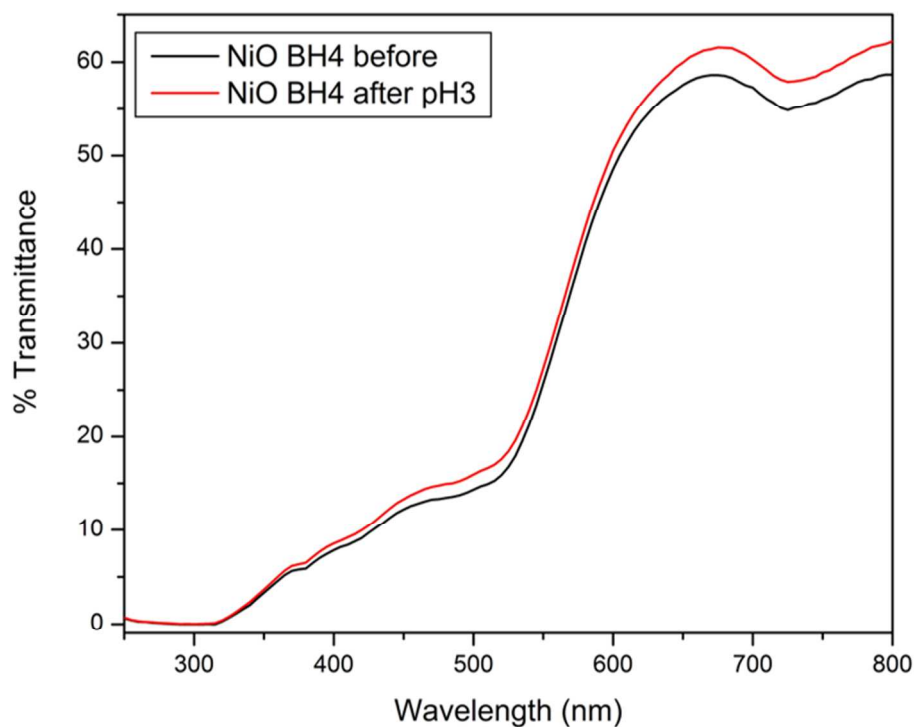


Figure S2. Sensitized BH<sub>4</sub> NiO film before and after 2.8 hours of light chopped chronoamperometry at an applied potential of 0 v vs. NHE in a pH 3 citric acid / citrate buffer with 5mM [Mo<sub>3</sub>S<sub>4</sub>]<sup>4+</sup>.

Solution	Ni (ppm)
pH 3 Buffer	< 0.25
Bare NiO	1.2
BH <sub>4</sub> Sensitized NiO	< 0.25

Table S1. ICP-OES results for 3 hour soak in pH 3 citrate/citric acid buffer of a bare NiO film and a BH<sub>4</sub> sensitized NiO film.

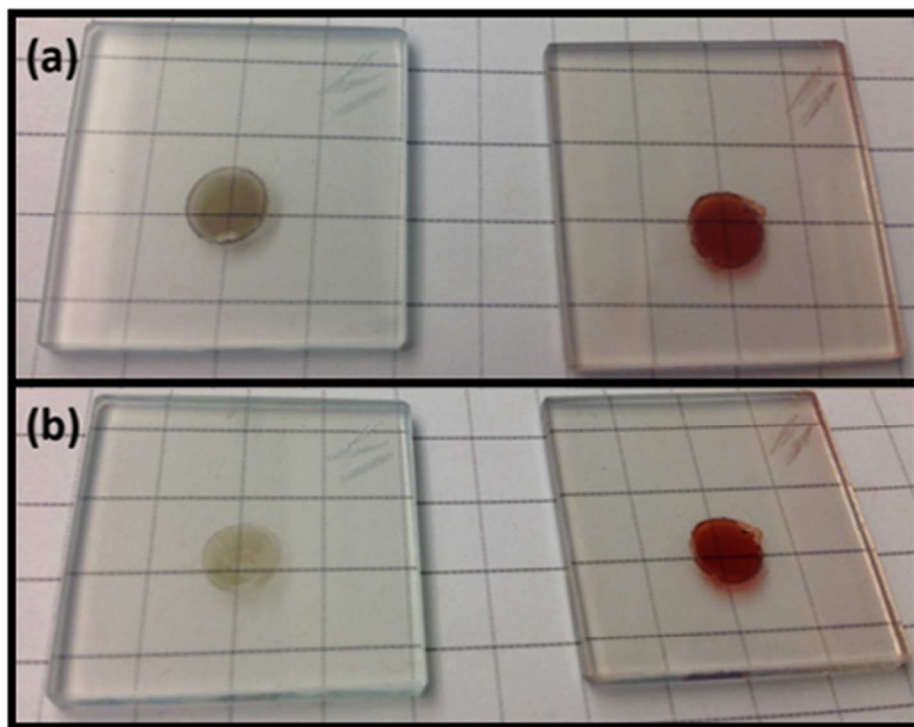


Figure S3. Bare NiO (left) and sensitized BH<sub>4</sub> NiO films (right) before (a) and after (b) soaking in a pH 3 citric acid / citrate buffer for 2.75 hours.

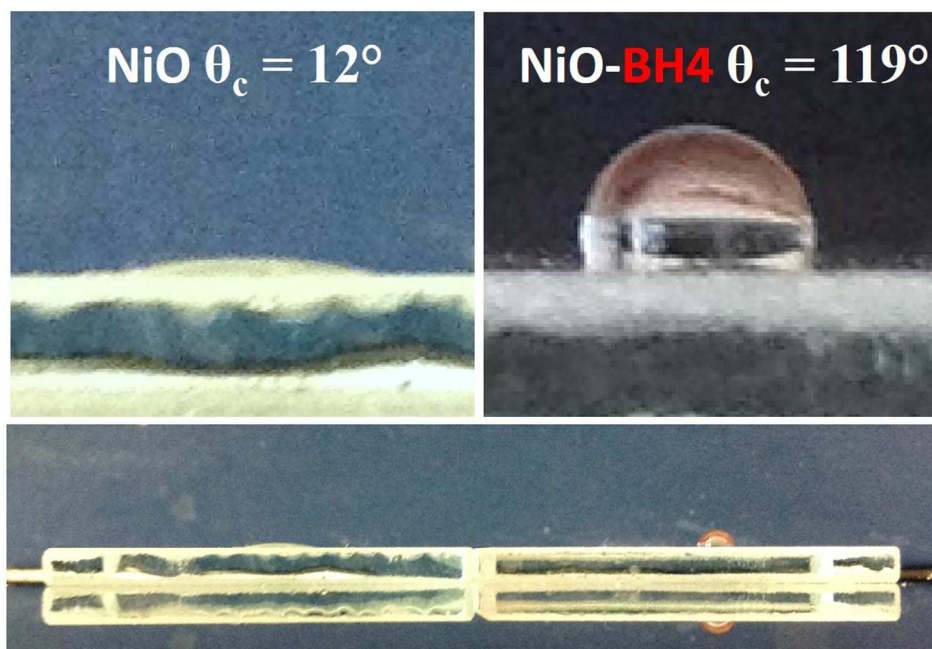


Figure S4. Contact angles for pH 0 (1M HCl) drop on bare NiO (left,  $\theta_c = 12^\circ$ ) and a BH<sub>4</sub> sensitized NiO film (right,  $\theta_c = 119^\circ$ ).

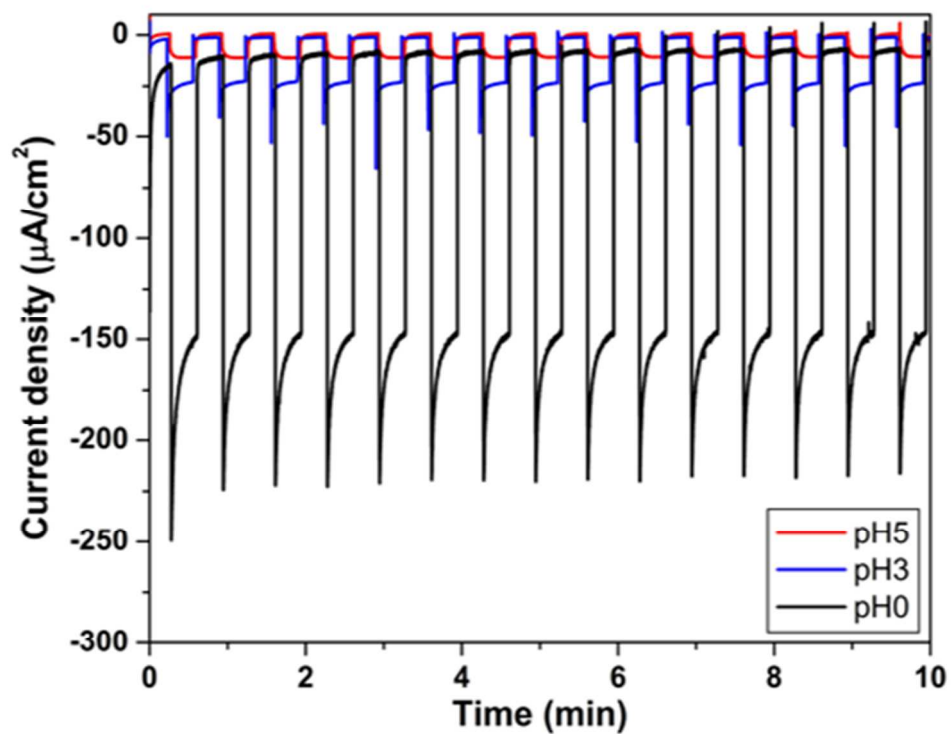


Fig. S5. Chronoamperometry of pH 5, 3 and 0 solutions all with 5mM  $[\text{Mo}_3\text{S}_4]^{4+}$  at an applied potential of 0 V vs. NHE.

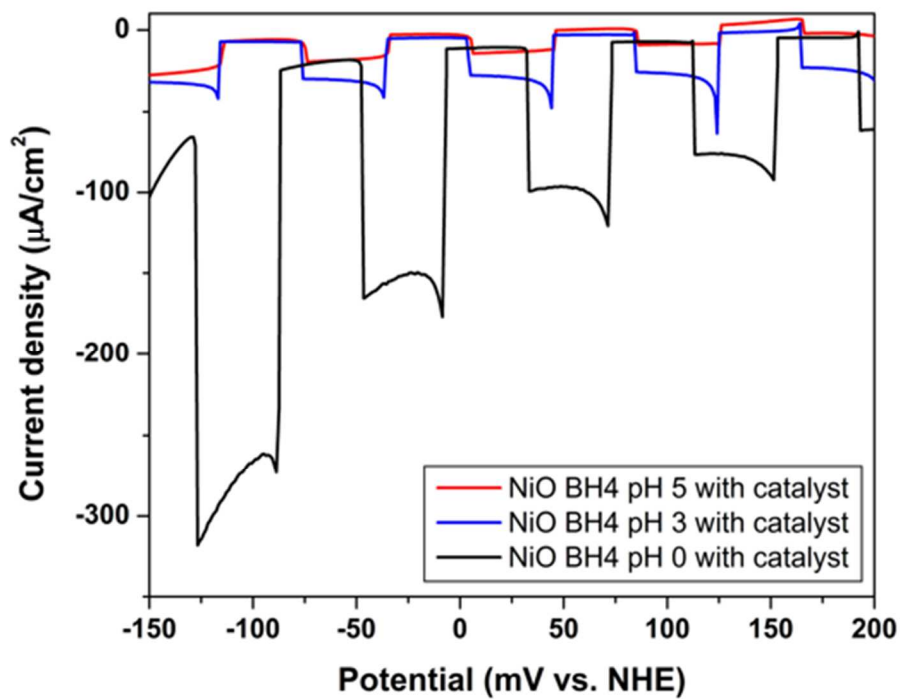


Fig. S6. Linear Sweep Voltammetry of pH 5, 3 and 0 solutions all with 5 mM  $[\text{Mo}_3\text{S}_4]^{4+}$  at an applied potential of 0 V vs. NHE with light chopping.

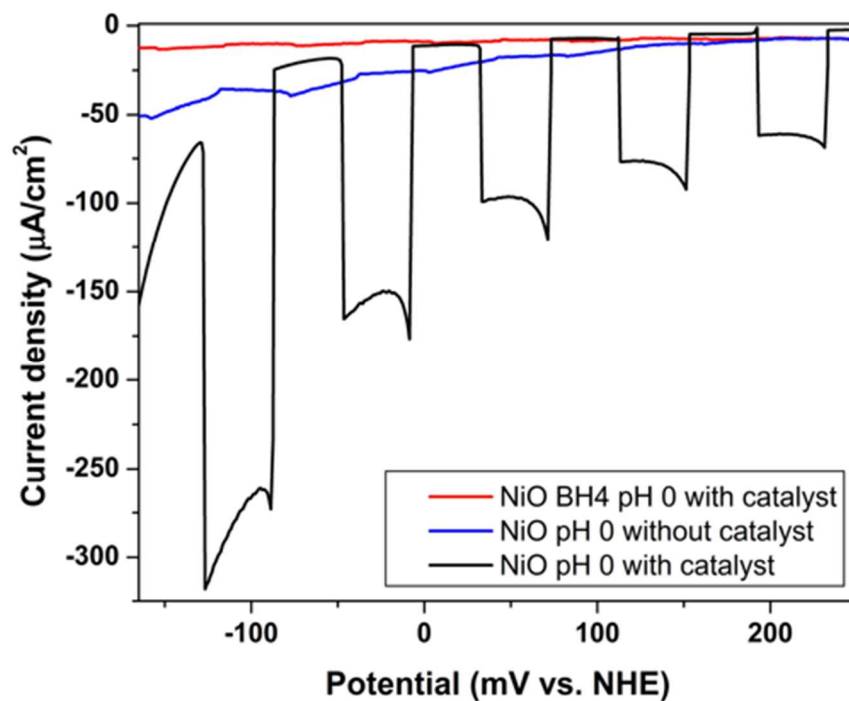


Fig. S7. Linear Sweep Voltammetry with light chopping of all pH 0 (1M HCl) solutions: BH<sub>4</sub> sensitized NiO with 5 mM [Mo<sub>3</sub>S<sub>4</sub>]<sup>4+</sup> (black trace). Bare NiO without [Mo<sub>3</sub>S<sub>4</sub>]<sup>4+</sup> (red trace). Bare NiO with 5 mM [Mo<sub>3</sub>S<sub>4</sub>]<sup>4+</sup> (blue trace).

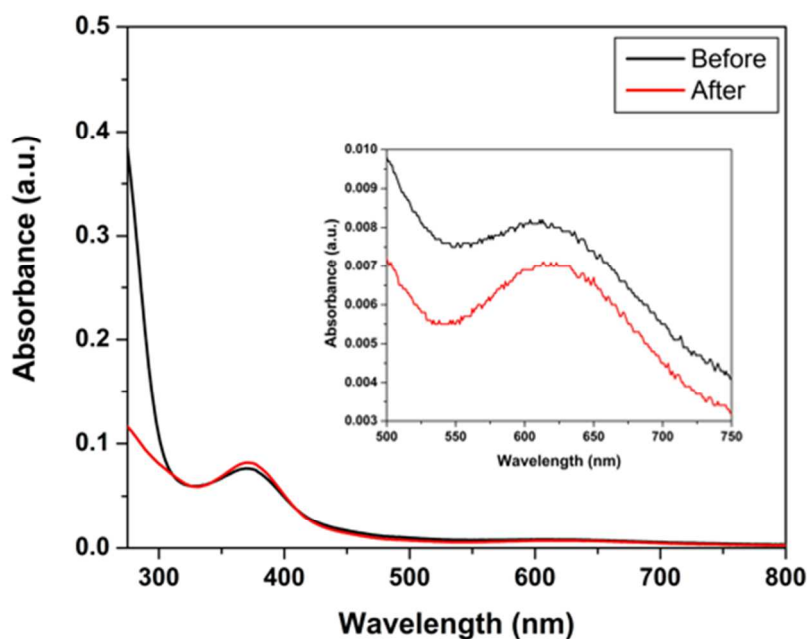


Figure S8. UV-Vis of the [Mo<sub>3</sub>S<sub>4</sub>]<sup>4+</sup> cluster before (black trace) and after (red trace) a 2.7 hour chronoamperometry experiment with constant light illumination held at 0 V vs NHE. Inset: A zoomed view of the absorption peak at 610 nm.

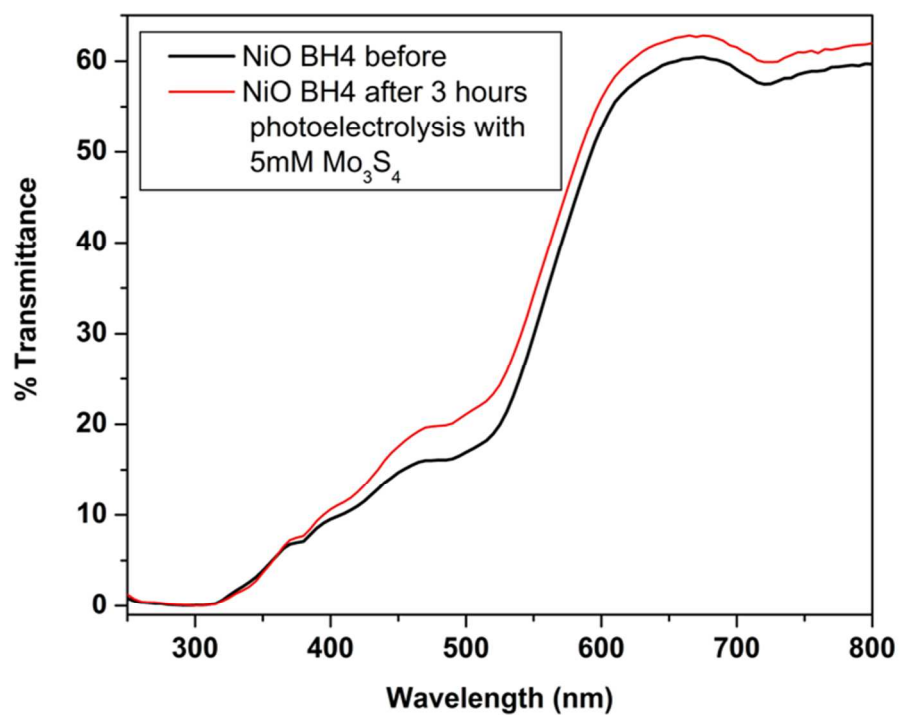
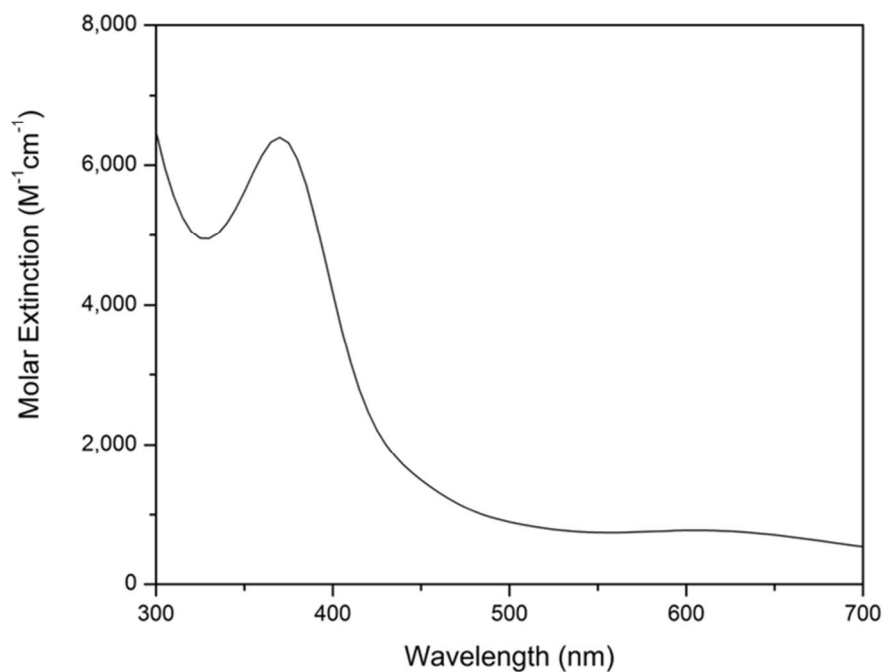


Figure S9. Transmittance of a BH<sub>4</sub> sensitized NiO film before (black trace) and after (red trace) 3 hours of photoelectrolysis of a pH 0 (1M HCl) solution with 5 mM [Mo<sub>3</sub>S<sub>4</sub>]<sup>4+</sup> at an applied potential of 0 V vs. NHE.



Characterization of [(Mo<sub>3</sub>S<sub>4</sub>)(H<sub>2</sub>O)<sub>9</sub>]Cl<sub>4</sub>

Figure S10. UV-Vis of [(Mo<sub>3</sub>S<sub>4</sub>)(H<sub>2</sub>O)<sub>9</sub>]Cl<sub>4</sub> in 2M HCl.

Trials	Current Density ( $\mu\text{A}/\text{cm}^2$ )	
	All Data	95% C.I.
1	139	
2	146	
3	150	
4	171	171
5	171	171
6	178	178
7	192	192
8	210	
9	214	
10	254	
Average	183	178
Standard Deviation	36	10

Table S2: Current densities of 10 experiments of  $\text{BH}_4$  sensitized NiO films with 5 mM  $[\text{Mo}_3\text{S}_4]^{4+}$  in pH = 0 electrolyte (1M HCl) at an applied potential of 0 V vs. NHE with a 300 W xenon lamp. The confidence interval (C.I.) at 95% is defined based upon the total trials, average, and standard deviation.

#### IPCE (Incident Photon to Current Efficiency)

The IPCE was calculated using the equation shown below where the light current was monitored at an applied potential of -0.170 V vs NHE while illuminating a  $\text{BH}_4$  sensitized NiO Film with 5mM  $[\text{Mo}_3\text{S}_4]^{4+}$  in pH = 0 (1M HCl) electrolyte with a ModuLight-Module from Ivium Technologies that contains 6 LEDs with wavelengths 460, 525, 590, 623, 660, 740 nm. The power density of the LEDs were determined using a optical power meter (model 1916-C) from Newport optics.

$$IPCE \% = \left( \frac{1240 \times J_{\text{Photocurrent}} \left( \frac{\text{mA}}{\text{cm}^2} \right)}{\text{Wavelength (nm)} \times I_{\text{Photon Power}} \left( \frac{\text{mW}}{\text{cm}^2} \right)} \right) \times 100$$

Where  $J_{\text{photocurrent}}$  is the photocurrent density measured at a specified wavelength,  $I_{\text{Photon Power}}$  is the incident power density at a specified wavelength.

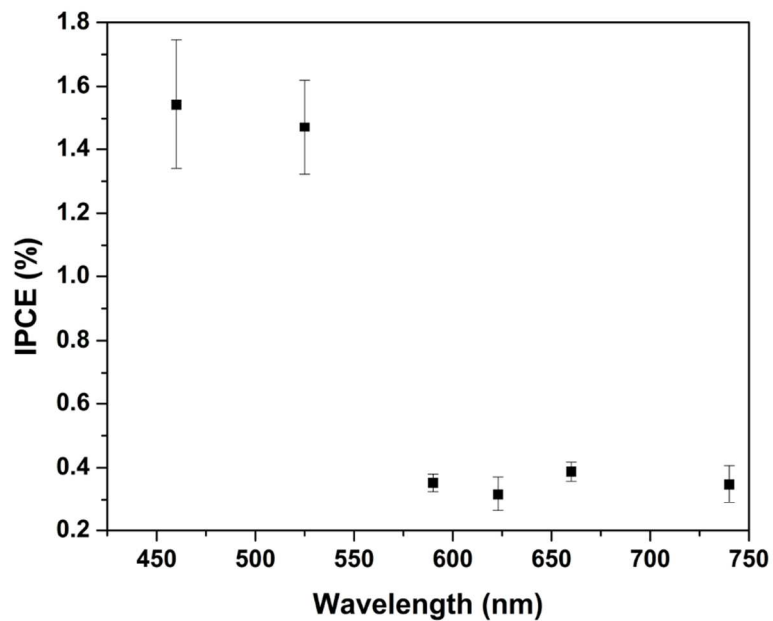


Figure S11. IPCE spectra of a BH<sub>4</sub> sensitized NiO Film with 5mM [Mo<sub>3</sub>S<sub>4</sub>]<sup>4+</sup> in pH = 0 (1M HCl) electrolyte at an applied potential of - 0.17 V vs NHE.

Wavelength	IPCE (%)
460	1.54 ± 0.20
525	1.47 ± 0.15
590	0.35 ± 0.027
623	0.32 ± 0.054
660	0.39 ± 0.030
740	0.35 ± 0.059

Table S3. Summary of IPCE results



Wavelength (nm)	Current ( $\mu\text{A}$ )	Current ( $\mu\text{A}/\text{cm}^2$ )	Power (mW)	Power ( $\text{mW}/\text{cm}^2$ )	IPCE (%)
Trial #1					
460	41.10	0.14679	62	24	1.62
525	19.67	0.07025	32	13	1.32
590	11.77	0.04204	59	23	0.38
623	8.82	0.03150	45	18	0.35
660	9.86	0.03521	44	17	0.38
740	6.55	0.02339	35	14	0.28
Trial #2					
460	42.98	0.15350	62	24	1.70
525	24.10	0.08607	32	13	1.61
590	10.07	0.03596	59	23	0.33
623	6.34	0.02264	45	18	0.25
660	9.32	0.03329	44	17	0.36
740	8.22	0.02936	35	14	0.36
Trial #3					
460	33.28	0.11886	62	24	1.31
525	22.14	0.07907	32	13	1.48
590	10.92	0.03900	59	23	0.35
623	8.52	0.03043	45	18	0.34
660	10.84	0.03871	44	17	0.42
740	9.25	0.03304	35	14	0.40

Table S4. Data to determine the average IPCE%.