

***Supporting Information***

**Photostable p-type dye-sensitized photoelectrochemical cells for water reduction**

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## **Materials and characterization.**

### **General information**

All reagents and solvents were purchased from Fisher Scientific Company and used without further purification. The silica gel (60 – 200  $\mu\text{m}$ ) and alumina (60 - 325 Mesh) were also purchased from Fisher Scientific. All products were characterized by  $^1\text{H}$  NMR (Bruker), and high resolution mass spectrometry (HRMS). All NMR spectra were obtained using a Bruker 250 or 400 MHz spectrometer. HRMS was conducted on a Bruker Daltonics BioTOF system with electrospray ionization (ESI) source.

### **Cyclic voltammetry**

The cyclic voltammetry measurements were conducted on a CV50W electrochemical workstation. The electrochemical cell consisted of a Pt working electrode, an Ag/AgCl in saturated KCl as the reference electrode, and a Pt wire auxiliary electrode in a single cell compartment. 0.1 M tetrabutylammonium perchlorate ( $\text{TBAClO}_4$ ) in DMF was used as the supporting electrolyte. The scan rate is 100 mV/s. The ferrocenium-ferrocene ( $\text{Fc}^{+/0}$ ) was used as the internal reference, and all potentials were reported relative to NHE using  $\text{Fc}^+/\text{Fc}$  couple (0.64 V versus NHE) as reference.

### **Film fabrication and characterization**

$\text{Ni}(\text{OH})_2$  sol was prepared following literature procedure by mixing  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and copolymer F108 in the mixture of ethanol and water. NiO film was made by doctor-blading method with scotch tape on each side of FTO glass. After dried in air, the film was heated in oven at 450  $^\circ\text{C}$  for 30 mins. The film area is proximately 1  $\text{cm}^2$ . This doctor-blading and heating procedure was reported 4 times. The film thickness is ca. 3

$\mu\text{m}$ . The atomic layer deposition of alumina was performed using a Picosun SunALE R-150B system. Trimethylaluminum (TMA) and water were used as sources of Al and O, respectively. The process was following our previous report (*Langmuir*, 2012, **28** (1), pp 950–956). The films were then soaked in dye solution (0.3 mM in  $\text{CH}_3\text{CN}$ ) for 16 hrs. After washed with  $\text{CH}_3\text{CN}$ , and dried under air. The electrode was then soaked in an aqueous solution of  $\text{Co(dmgBF}_2\text{)}$  for 5 minutes to load Cobalt catalyst. The absorption spectra were measured by Lambda 950 spectrophotometer (Perkin-Elmer).

### **Photoelectrochemistry and GC measurement**

The photoelectrochemistry was carried out in our homemade PEC cell with the three electrodes in one compartment. The NiO film electrode, Ag/AgCl in sat. aq. KCl, and Pt were used as the working, reference and counter electrode respectively. The cell was degassed for 20 minutes by flushing Ar prior to each measurement. The electrode was illuminated with 300W Xe lamp equipped with both water jet to eliminate IR illumination and 420 nm long pass filters to avoid direct bandgap illumination of NiO. The LSV was performed by applying bias on the working electrode. The produced hydrogen was measured using a gas chromatography (Shimadzu) equipped with a pulsed discharge helium ionization detector (PDHID) detector. The GC was calibrated with known amounts of hydrogen produced by electrolysis using a Pt mesh as the working electrode. All potentials were converted and reported to values versus NHE (the potential of Ag/AgCl was determined as 0.2 V vs. NHE by using Fc reference).

### **Incident photon to current conversion spectrum (IPCE)**

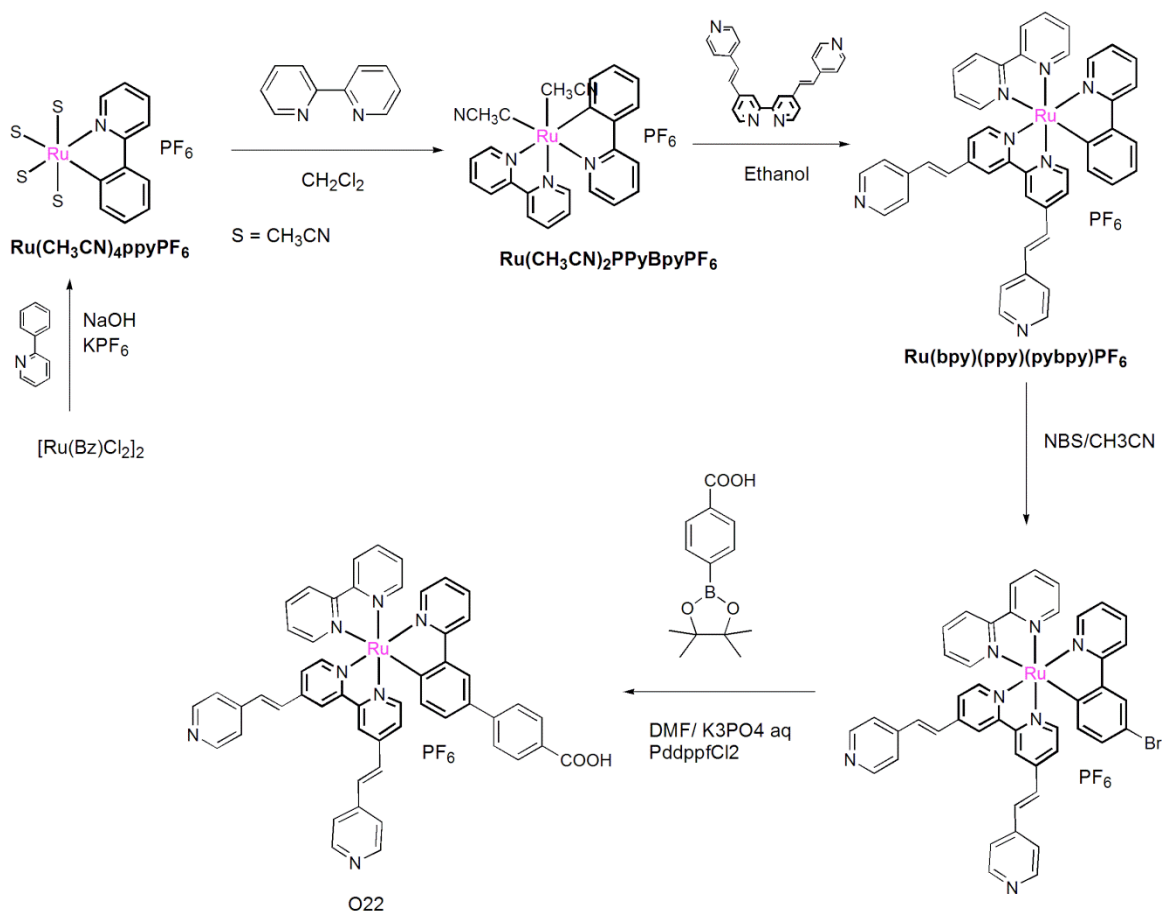
The incident photon to current conversion efficiency (IPCE) spectra of the devices using the bare NiO, the O22 sensitized NiO electrode, or the NiO electrode

loaded with O<sub>2</sub> and CodmgBF<sub>2</sub> assembly were determined in our one-compartment PEC cell. The electrode was illuminated by a 300 W Xenon lamp equipped with an Oriel Cornerstone 130 1/8 M monochromator from Newport. The power density of the monochromatic light was determined using a Newport optical power meter (model 1830-c) with a diode detector. The experiment was performed with an applied bias of 0.1 V vs. NHE. The IPCE value was calculated by the equation:  $IPCE\% = \frac{I_{ph}(\lambda) \times 1240}{P(\lambda) \times \lambda(\text{nm})} \times 100$ , where  $I_{ph}$  is the photocurrent density,  $P$  is the incident power, and  $\lambda$  is the incident light wavelength.

### **Binding determination**

The binding of Ru(bpy)(ppy)(pybpy)PF<sub>6</sub> to CodmgBF<sub>2</sub> were determined by the UV-vis titration. A stock solution of Ru(bpy)(ppy)(pybpy)PF<sub>6</sub> (9.8E-5 M in CH<sub>3</sub>CN) were prepared. A distinct red shift from 571 nm to 593 nm, and the enhanced absorption were observed upon addition of CodmgBF<sub>2</sub> (figure S2). The association constant was calculated from the plot of absorption change versus the concentration of CodmgBF<sub>2</sub> (Figure S2).

### **Synthesis**



### Dichloro(Benzene)ruthenium dimer $[\text{Ru}(\text{Bz})\text{Cl}_2]_2$

Ruthenium chloride (2.0 g) was suspended in 100 mL 90% Ethanol. 1,3-cyclohexadiene (9.5 mL) was dropwise added. The mixture was heated at 95 °C for 7 hrs. The red precipitate was filtered out, and washed with ethanol, and dried under vacuum. The product was used without further purification.

### $\text{Ru}(\text{ppy})(\text{CH}_3\text{CN})_4\text{PF}_6$

$[\text{Ru}(\text{Bz})\text{Cl}_2]_2$  (1.0 g, 2 mmol), NaOH (0.16 g, 4 mmol), Phenylpyridine (0.62 g, 4 mmol), and  $\text{KPF}_6$  (1.47 g, 8 mmol) were stirred in 30 mL  $\text{CH}_3\text{CN}$ . The mixture was degassed, and stirred at 45 °C for 20 hrs. The mixture was filtered and the solvent was evaporated.

The residue was purified on  $\text{Al}_2\text{O}_3$  column by mixture of  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (9/1, v/v). The yellow fraction was collected, and the solvent was evaporated. The residue was recrystallized in  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ . Yield: 1.79 g (79%)  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.93 (1 H, d,  $J = 6.4$  Hz), 8.00 (1 H, d,  $J = 7.6$  Hz), 7.90 (1H, d,  $J = 8.4$  Hz), 7.60 (2 H, m), 7.18 (1 H, d,  $J = 7.6$  Hz), 7.11 (1 H, d,  $J = 7.6$  Hz), 6.97 (1 H, d,  $J = 7.6$  Hz), 2.54 (3H, s), 2.04 (6 H, s).

$\text{Ru}(\text{ppy})(\text{bpy})(\text{CH}_3\text{CN})_2\text{PF}_6$

$\text{Ru}(\text{ppy})(\text{CH}_3\text{CN})_4\text{PF}_6$  (451 mg, 0.8 mmol ) and 2,2'-bipyridine (125 mg, 0.8 mmol) were added in 30 mL  $\text{CH}_2\text{Cl}_2$ . The mixture was stirred at rt for 20 hrs. After solvent was removed, the residue was purified on  $\text{Al}_2\text{O}_3$  column using  $\text{CH}_2\text{Cl}_2$  as eluent. The title compound was purified by recrystallization in  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  to give purple product. Yield: 441 mg, 86%.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  9.39 (1H, d,  $J = 6$  Hz), 8.48 (1 H, d,  $J = 8.0$  Hz), 8.13 (3 H, m), 7.92 (4H, m), 7.70 (1 H, t,  $J = 8.0$  Hz), 7.59 (1 H, t,  $J = 7.2$  Hz), 7.38 (1 H, d,  $J = 4.8$  Hz), 7.28 (1 H, d,  $J = 7.2$  Hz), 7.05 (2H, m), 6.76 (1H, t,  $J = 7.2$  Hz), 2.25 (3H, s), 2.20 (3 H, s).

$\text{Ru}(\text{ppy})(\text{bpy})(\text{pybpy})\text{PF}_6$

$\text{Ru}(\text{ppy})(\text{bpy})(\text{CH}_3\text{CN})_2\text{PF}_6$  (115 mg, 0.18 mmol) and pybpy (66.2 mg, 0.18 mmol) were added to 50 mL ethanol. The mixture was heated to reflux for 2 hrs. After the mixture was cooled to rt, the solvent was removed. The mixture was purified on silica gel column eluted with a mixture of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{aq. KNO}_3$ .  $^1\text{H}$  NMR (400 MHz, Acetone):  $\delta$  6.49

(1H, d, J= 6 Hz), 6.93 (2H, m), 7.06 (1H, t, J= 7.2 Hz), 7.41 (2H, m), 7.60 (1H, d, J = 6 Hz), 7.06-7.81 (10 H, m), 7.96 (6H, m), 8.08 (1H, d, J = 6 Hz), 8.19 (1H, d, J = 5.6 Hz), 8.62 (2H, d, J = 8 Hz), 8.80 (4H, m), 9.03 (1H, m), 9.12 (1H, m) ppm. Yield: 81%.  
ESI\_MS([M-PF<sub>6</sub>]<sup>+</sup>):774.1.

#### Ru(ppy-Br)(bpy)(pybpy)PF<sub>6</sub>

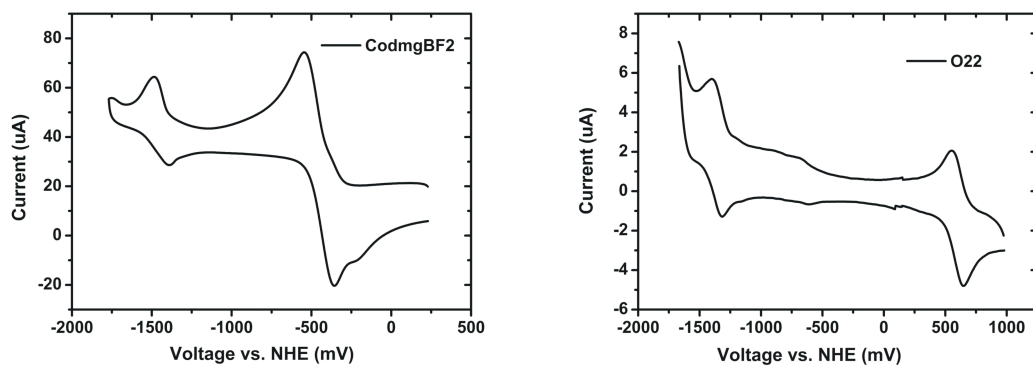
Ru(ppy)(bpy)(pybpy)PF<sub>6</sub> (44 mg, 0.048 mmol) and NBS(8.9 mg, 0.05 mmol) were added in 50 mL CH<sub>3</sub>CN. The mixture was stirred overnight. NH<sub>4</sub>NH<sub>4</sub>·H<sub>2</sub>O (10 mg) was added to quench the reaction. After solvent was evaporated, the mixture was recrystallized in CH<sub>3</sub>CN/Et<sub>2</sub>O. Yield: 31.8 mg. (66%) ESI\_MS([M-PF<sub>6</sub>]<sup>+</sup>): 854.0, [M+1-PF<sub>6</sub>]<sup>2+</sup>: 427.5.

#### O22

Ru(ppy-Br)(bpy)(pybpy)PF<sub>6</sub> (31.8 mg, 0.032 mmol) and 4-carboxylphenylboronic acid pinacol ester (11.9 mg, 0.048 mmol) were added into DMF (10 mL). The mixture was degassed for 20 mins. Pd(dppf)Cl<sub>2</sub> (5 mg), and K<sub>2</sub>CO<sub>3</sub> (44 mg, 0.32 mmol) were added. The mixture was heated at 85 ° C under Ar for 24 hrs. After the mixture was cooled to room temperature, the mixture was filtered. The filtrate was collected, and the solvent was evaporated. The product was purified by recrystallization in CH<sub>3</sub>CN/Et<sub>2</sub>O, and washed with large amount of Et<sub>2</sub>O. <sup>1</sup>H NMR (400 MHz, Acetone): δ 6.69 (1H, d, J= 4.8 Hz), 6.84 (1H, m), 7.12 (1H, t, J= 7.2 Hz), 7.19 (1H, d, J = 8 Hz), 7.29 (1H, d, J = 6 Hz), 7.43 (2H, m), 7.59-7.63 (6 H, m), 7.68-7.74 (3H, m), 7.82-7.88 (4H, m), 8.97 (3H, m),

8.05 (3H, m), 8.23 (1 H, d, J = 12 Hz), 8.39 (1H, m), 8.44 (1H, d, J = 6 Hz), 8.62-8.68 (6H, m), 8.98 (1H, m), 9.08 (1H, m) ppm. Yield: 65%. ESI\_MS([M-PF<sub>6</sub>]<sup>+</sup>): 894.1.

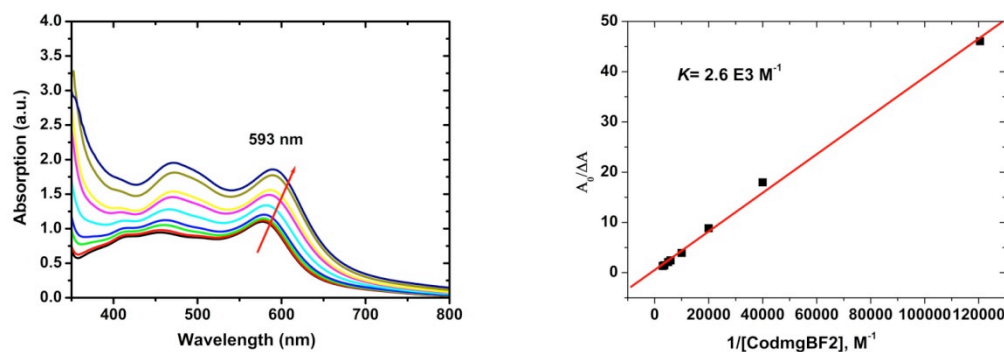




**Figure S1.** (Left) the CV voltammogram of CodmgBF<sub>2</sub>. (Right) the CV voltammogram of O22. All CVs were measured in DMF with 0.1 M TBAP as the supporting electrolyte.

**Table S1.** The redox potentials of O22 and CodmgBF<sub>2</sub> determined from cyclic voltammetry. All potentials are reported versus NHE.

	$E_{\text{ox}}$ (V)	$E_{\text{red}}$ (V)
O22	0.60	-1.36
CodmgBF <sub>2</sub>		-0.46



**Figure S2.** (Left) the absorption spectra of Ru(bpy)(ppy)(pybpy)PF<sub>6</sub> upon addition of CodmgBF<sub>2</sub>. The arrow indicates the spectrum shift. (Right) the Job plot of absorption change versus the concentration of CodmgBF<sub>2</sub>.

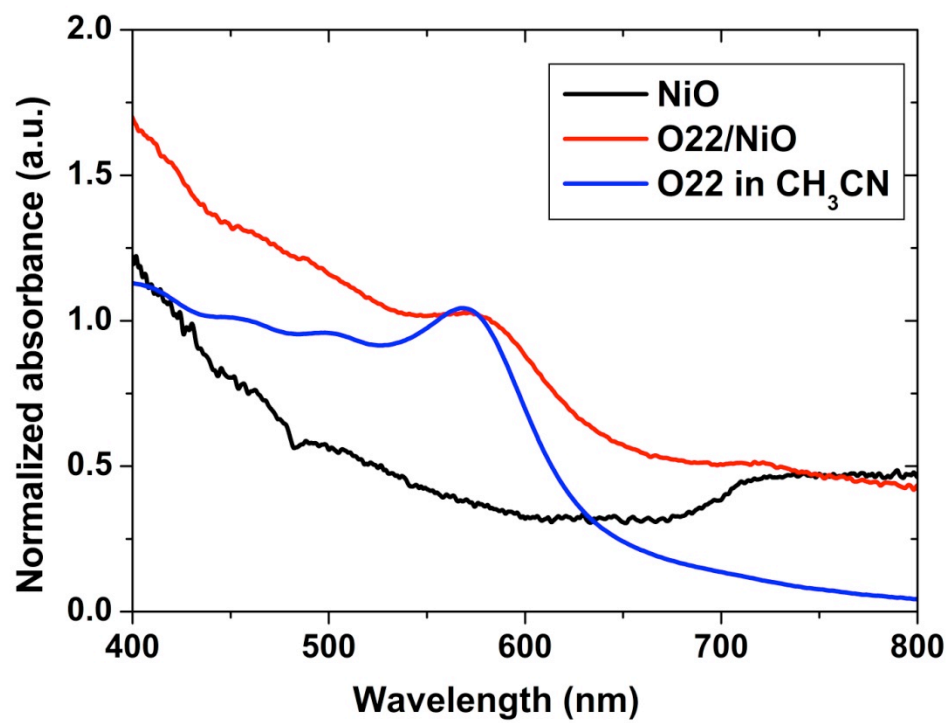


Figure S3. The absorption spectra of O22 in CH<sub>3</sub>CN, the bare NiO film, and the O22 sensitized NiO films.

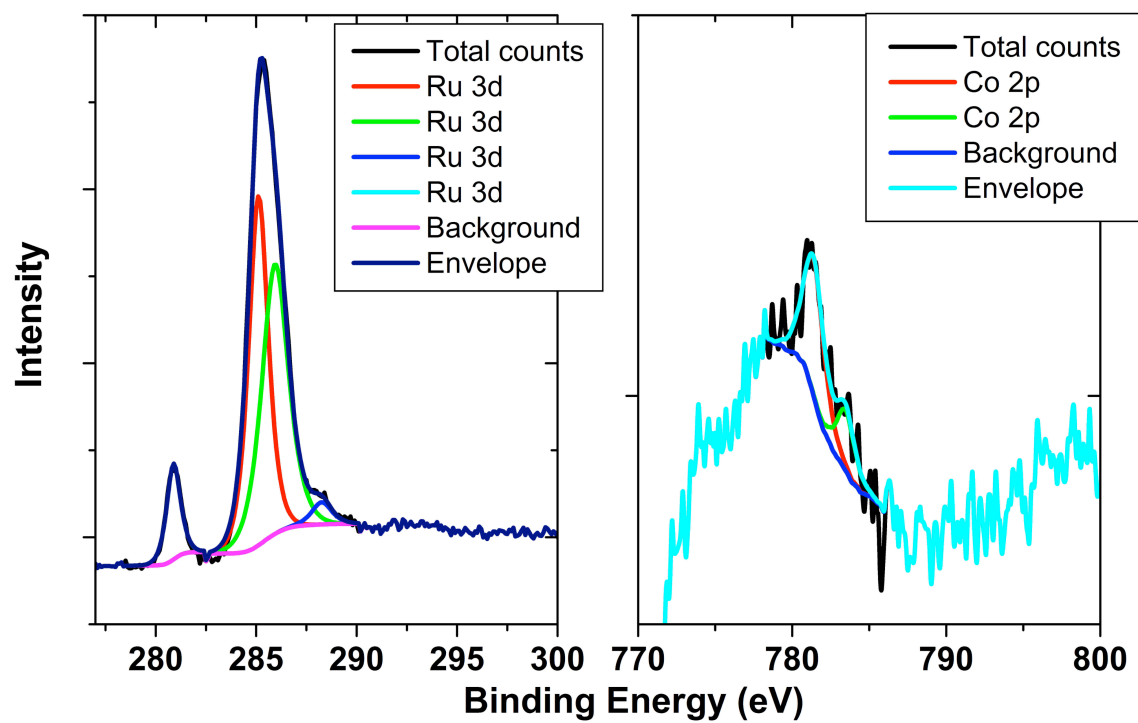


Figure S4. XPS results of the O22 and CodmgBF2 sensitized NiO films.

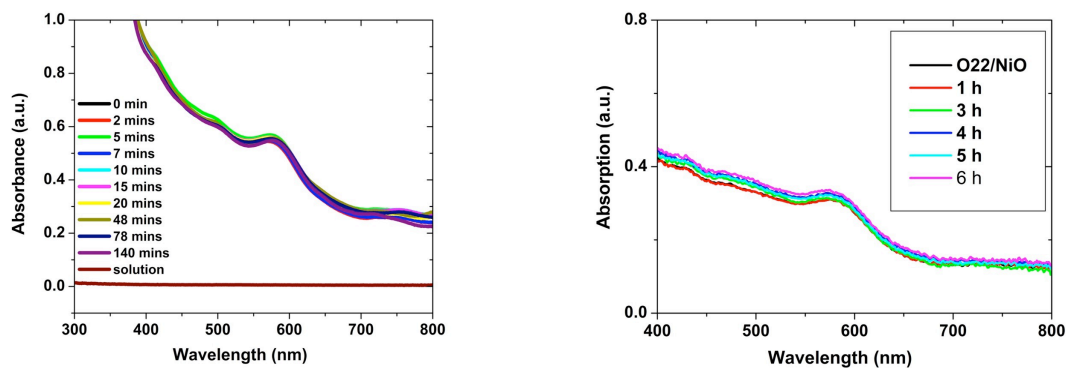
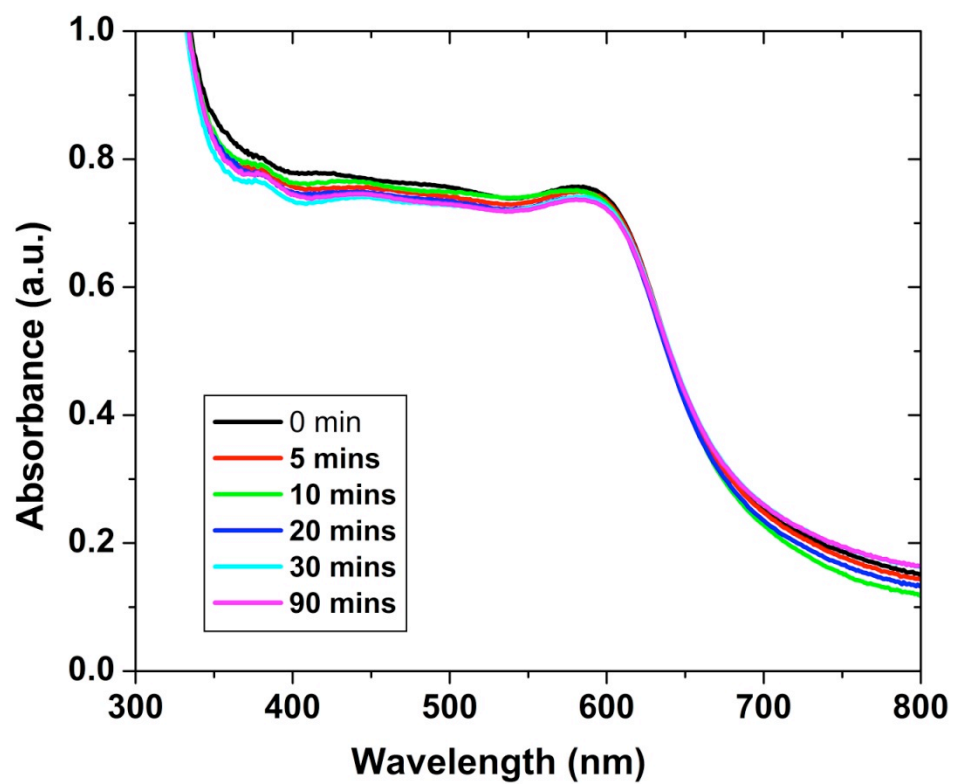
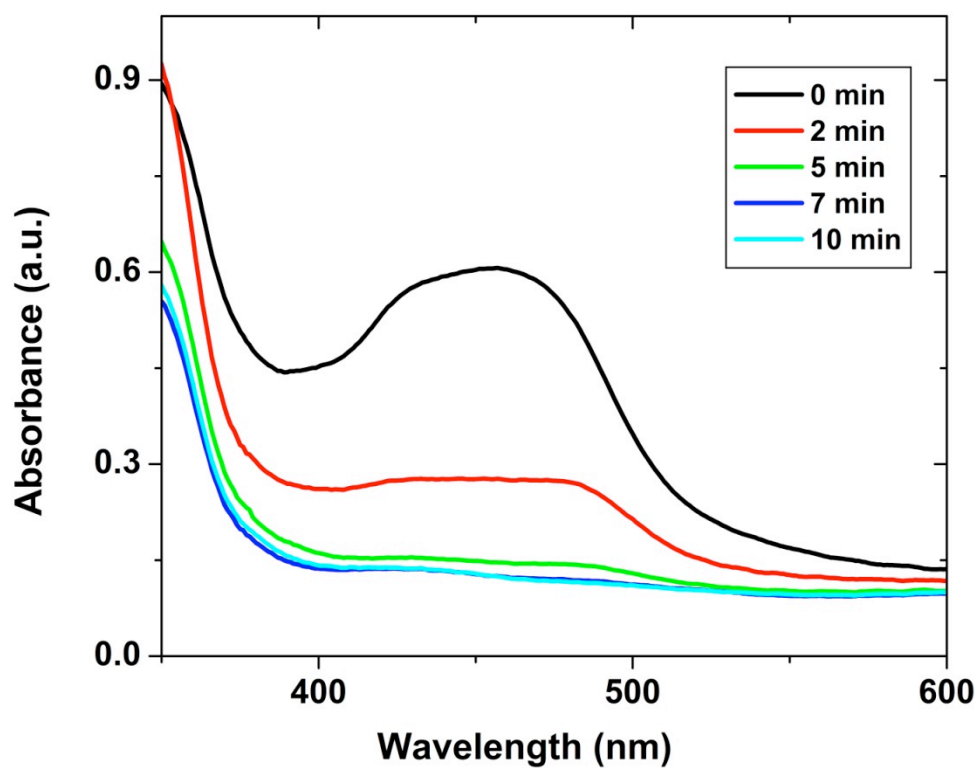


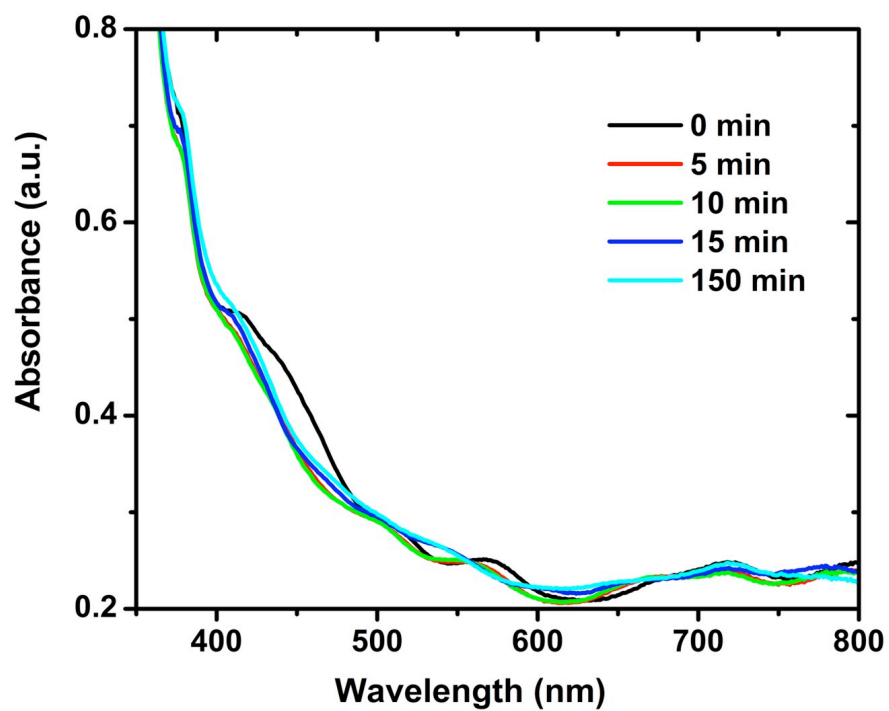
Figure S5. (Left) The absorption spectra of the O22/NiO film in neutral water. The legend shows the soaking time. All experiments were performed in dark. (Right) The absorption spectra of the O22/NiO film. The film was soaked in the pH 7 buffer solution comprising 0.1 M  $\text{KH}_2\text{PO}_4$  and 0.4 M  $\text{Na}_2\text{CO}_3$  for different times as indicated.



**Figure S6.** The absorption spectra of O<sub>22</sub>/TiO<sub>2</sub> film. The film was soaked in neutral water for different times as indicated.

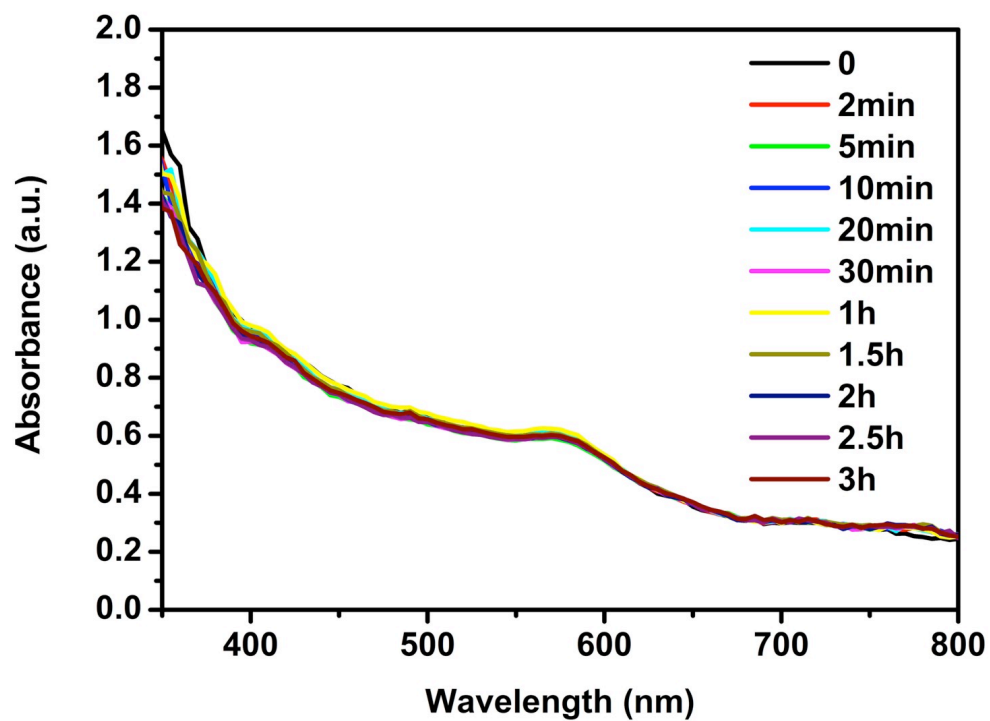


**Figure S7.** The absorption spectra of Ru(bpy)<sub>2</sub>(dcb)Cl<sub>2</sub>/TiO<sub>2</sub> film. The film was soaked in neutral water for different times as indicated.

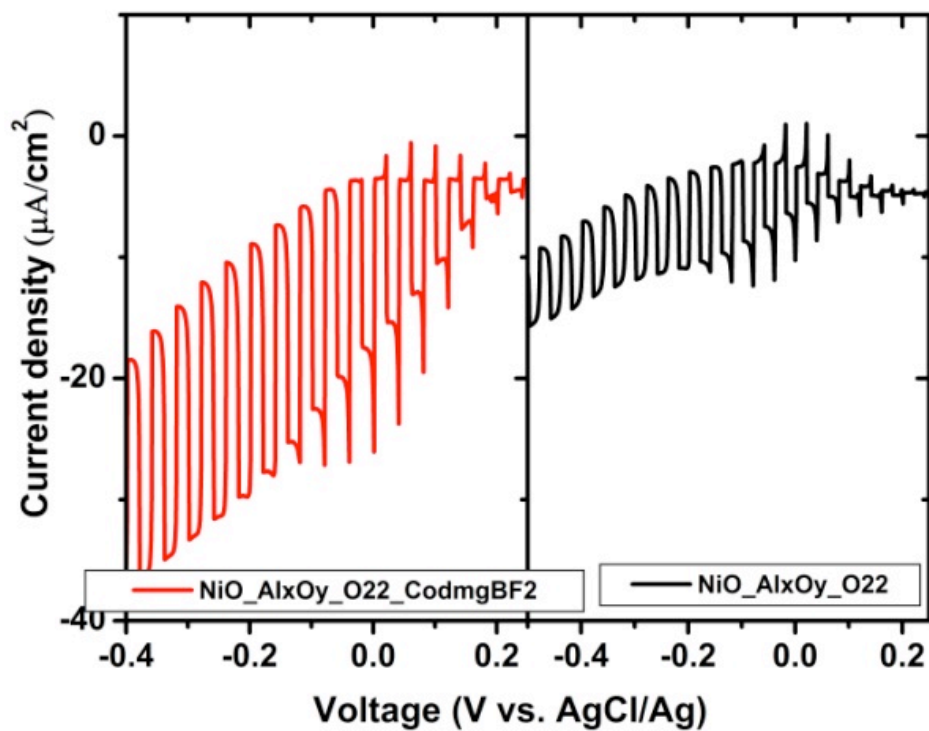


**Figure S8.** The absorption spectra of the Ru(dcb)(bpy)<sub>2</sub>Cl<sub>2</sub>/NiO film. The film was soaked in neutral aqueous solution for different times as indicated.

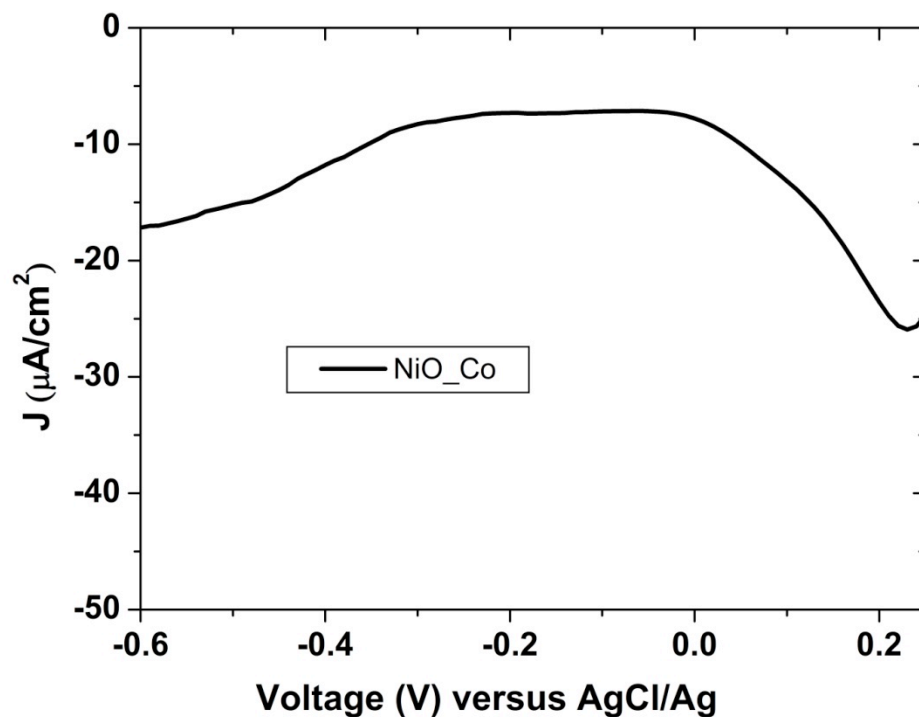




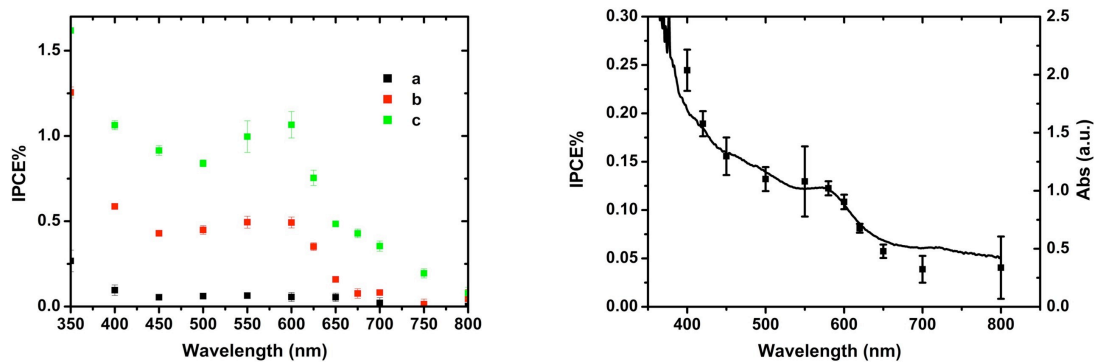
**Figure S9.** The absorption spectra of the O22 sensitized alumina coated NiO film. The film was soaked in the pH 7 aqueous solution for different times as indicated.



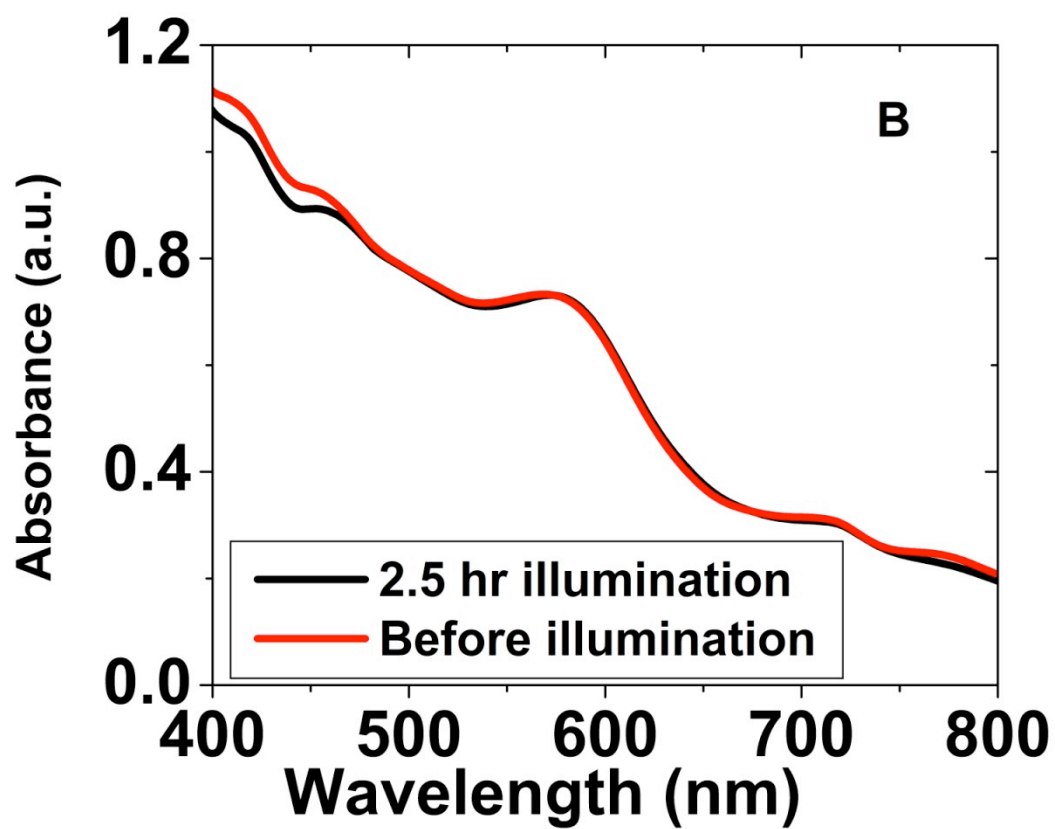
**Figure S10.** LSV of the NiO electrode with AlxOy coating (with and without CodmgBF<sub>2</sub> catalyst). The scan direction is from positive potential to negative potential. The scan rate is 1 mV/s.



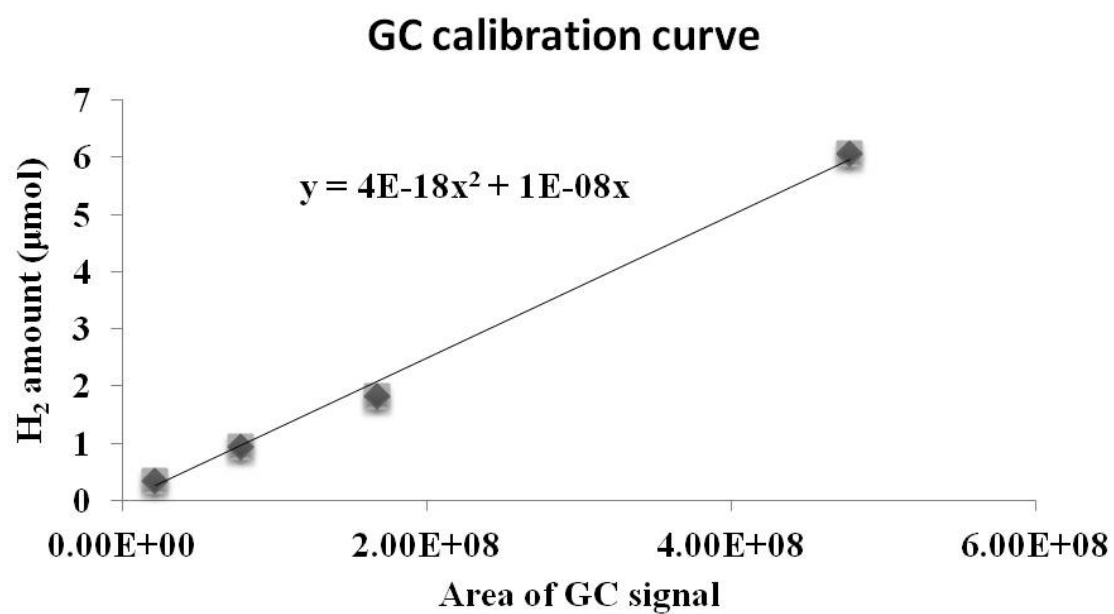
**Figure S11.** The LSV of the NiO film loaded with only CodmgBF<sub>2</sub> catalyst under the chopped light illumination. The scan direction is from positive to negative. The on and off time of the chopping is 20 s. No photocurrent has been observed in this measurement confirming that the photocurrent of our PEC studies is produced by the sensitization of O<sub>2</sub>, which is also consistent with the IPCE measurements.



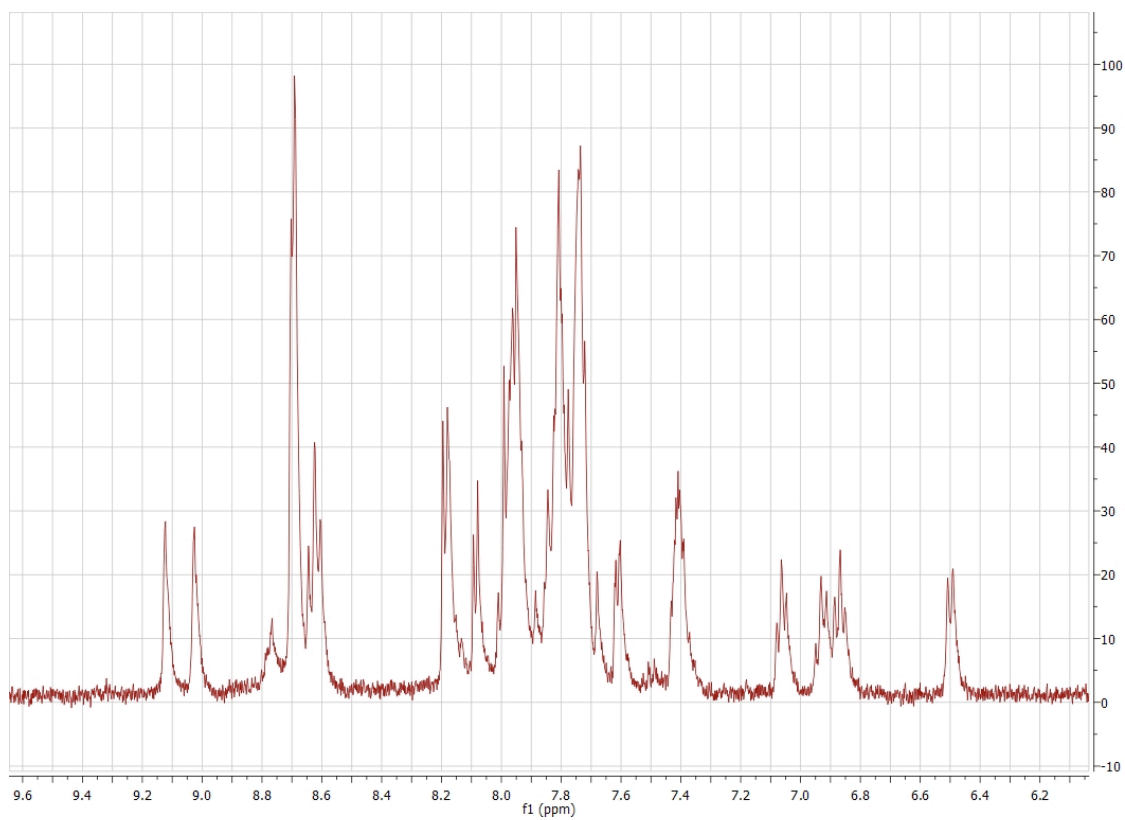
**Figure S12.** (Left) The IPCE spectra of the bare NiO (a), the O22/NiO electrode (b), and the NiO electrode loaded with O22-CodmgBF<sub>2</sub> assembly at an applied bias of 0.1 V (vs. NHE). (Right) The IPCE spectrum of the O22/NiO electrode at an applied bias of 0.1 V (vs. NHE) (square, left axis), and the absorption spectrum of the O22 sensitized NiO film (black line).



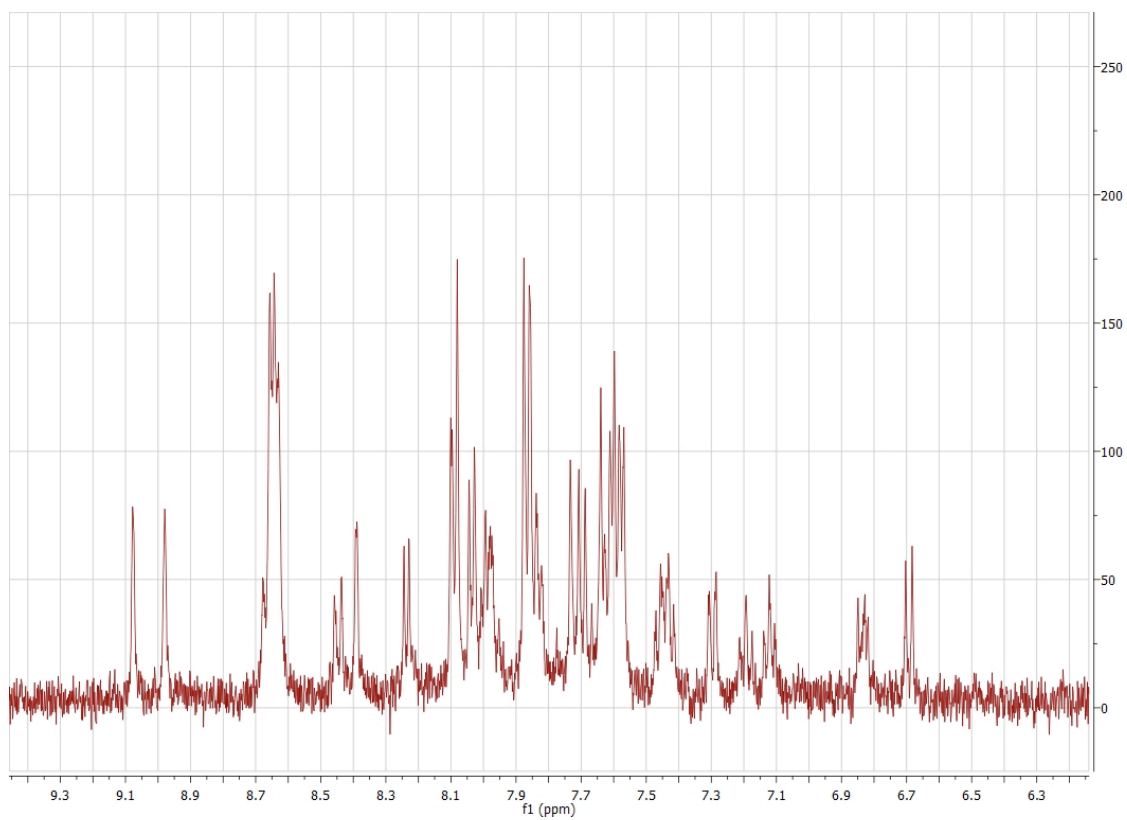
**Figure S13.** The absorption spectra of the photoelectrode before and after 2.5 hr PEC measurement.



**Figure S14.** The calibration curve of GC.



**Figure S15.**  $^1\text{H}$  NMR spectrum of  $\text{Ru(ppy)(bpy)(pybpy)PF}_6$  in  $\text{d}_6$  Acetone.



**Figure S16.**  $^1\text{H}$  NMR spectrum of O22 d6 Acetone.