

## Supplementary Information

### Materials:

**Co1** and **P1** were synthesized as previously described in literatures (for **Co1**: A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1984, **106**, 5197. For **P1**: P. Qin, H. Zhu, T. Edvinsson, G. Boschloo, A. Hagfeldt and L. Sun, *J. Am. Chem. Soc.*, 2008, **130**, 8570.). The pH 7.0 phosphate buffer solution (50 mM) was used as received from Aldrich.

### Device fabrication:

NiO films were prepared according the published procedure (L. Li, E. A. Gibson, P. Qin, G. Boschloo, M. Gorlov, A. Hagfeldt and L. Sun, *Adv. Mater.*, 2010, **22**, 1759). The NiO film electrodes (1 cm<sup>2</sup> active area) with 1.5 μm thickness were dipped into a 0.2 mM dye bath overnight for sensitization. After washing with ethanol and drying by air flow, catalyst **Co1** was introduced by dropping acetonitrile solution of **Co1** (100 μl, 2mM) onto the surface of **P1** sensitized NiO, followed by drying with dry air flow. The device was charged with pH 7.0 phosphate buffer solution (50 mM) and flushed with argon for 20 minutes prior to use.

### Experimental techniques:

The photocurrent measurements were carried out in a standard three-electrode cell with an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie), using the above prepared photo-cathode as the working electrode, Ag/AgCl in 3M KCl as reference electrode and a platinum wire as the counter electrode. A -400 mV vs Ag/AgCl potential was carried out on the working electrode. The device was charged with pH 7.0 phosphate buffer solution (50 mM) and flushed with argon for 20 minutes prior to use. The photocathode was illuminated using a light emitting diode array to give a light intensity of 250 Wm<sup>-2</sup> calibrated by a OPHIR Nova II Laser

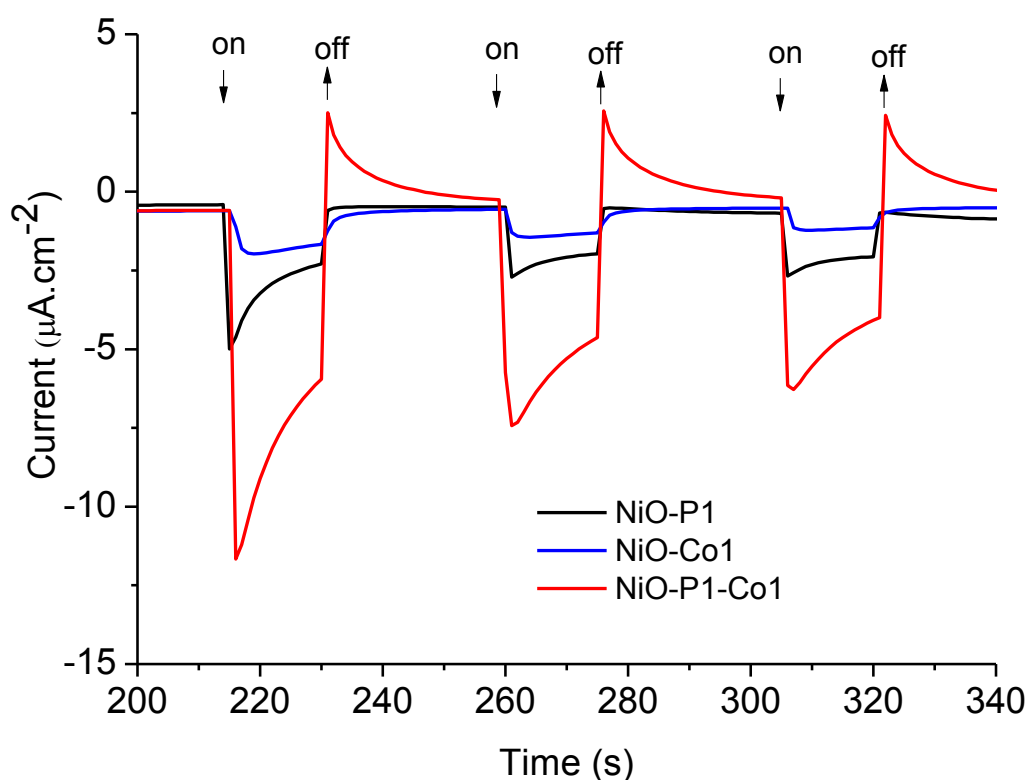
power meter connected with a thermopile sensor (OPHIR, 3A-P-FS). After illumination on the photocathode for 30 min, 1 mL of electrolyte in the PEC was transferred into a modified oxygen Clark electrode to evaluate hydrogen using a Hamilton SampleLock syringe. Each results were repeated for at least three times.

The hydrogen evolution was recorded by a modified oxygen Clark electrode disc, which was manufactured according the guidance from Hansatech instruments. For oxygen measurement, there is a platinum electrode set in the central dome as the cathode, while a silver electrode in the floor of the disc as the anode. For hydrogen measurement, the anode is platinum black and the cathode is silver chloride. Conversion of an oxygen electrode disc for H<sub>2</sub> measurement is mainly based on the following steps. First, the platinum electrode is plated using 2M sulphuric acid H<sub>2</sub>SO<sub>4</sub> as the electrolyte for 10 minutes, followed by plating using 2% chloroplatinic acid H<sub>2</sub>PtCl<sub>6</sub> as the electrolyte for 40 minutes. Secondly, silver is plated using sufficient saturated silver chloride solution for 20 minutes. Between each step, the disc should be gently washed with sufficient distilled water.

For the photochemical hydrogen generation, the reaction system was cooled by a circulate water system. For the homogenous system, the concentration of sensitizer and the catalyst were **P1** ( $5 \times 10^{-5}$  M) and **Co1** ( $2 \times 10^{-4}$  M) respectively. Generally, a degassed acetonitrile solution of catalyst **Co1** was injected using a syringe through a septum into 5% TEOA in 1:1 MeCN/H<sub>2</sub>O solution prior adjusted pH 7 using HCl, after degassing for 20 minutes. The above solution was irradiated by a 500 W xenon light source through a 400 nm cut off filter.

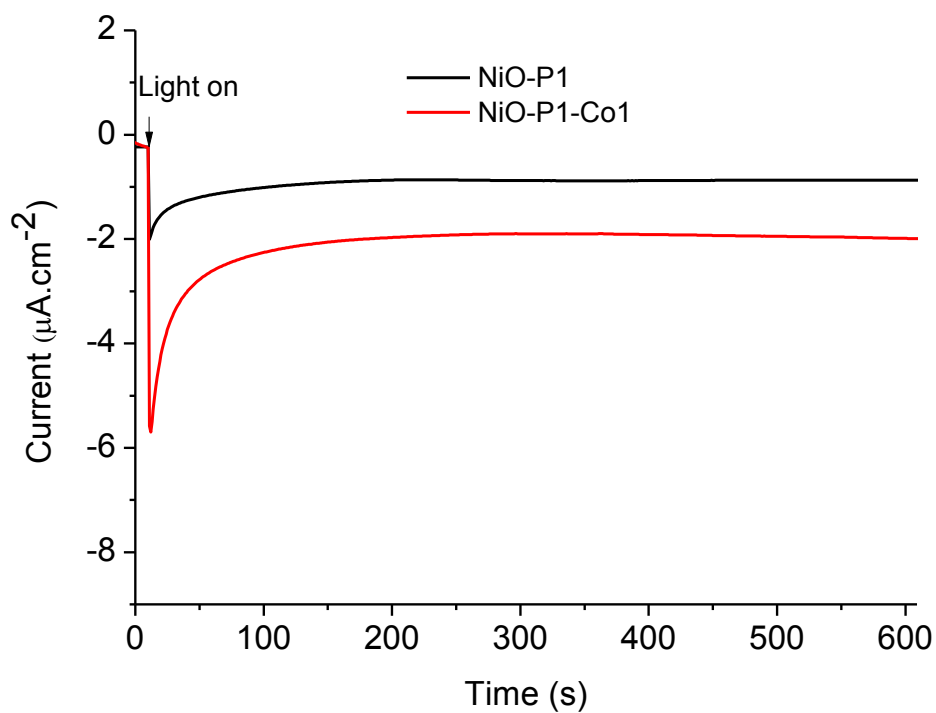
GC-2014, Shimadzu (Molecular sieve 5A, TCD detector, nitrogen as carry gas) was used to confirm the hydrogen generated in the homogenous system.

In figure 2 (main text), it was noticed that the baselines for the cathodes (NiO-Co1 and NiO-P1-Co1) are different with the cathode (NiO-P1). However, this behavior is not found in 0.1 M CH<sub>3</sub>COONa (pH 7.0) solution (figure S1). This difference between the baselines is probably due to the impact of the electrolyte. In addition, the photocathodes was illuminated for another 600 s to discover the photocurrent decay (figure S2).



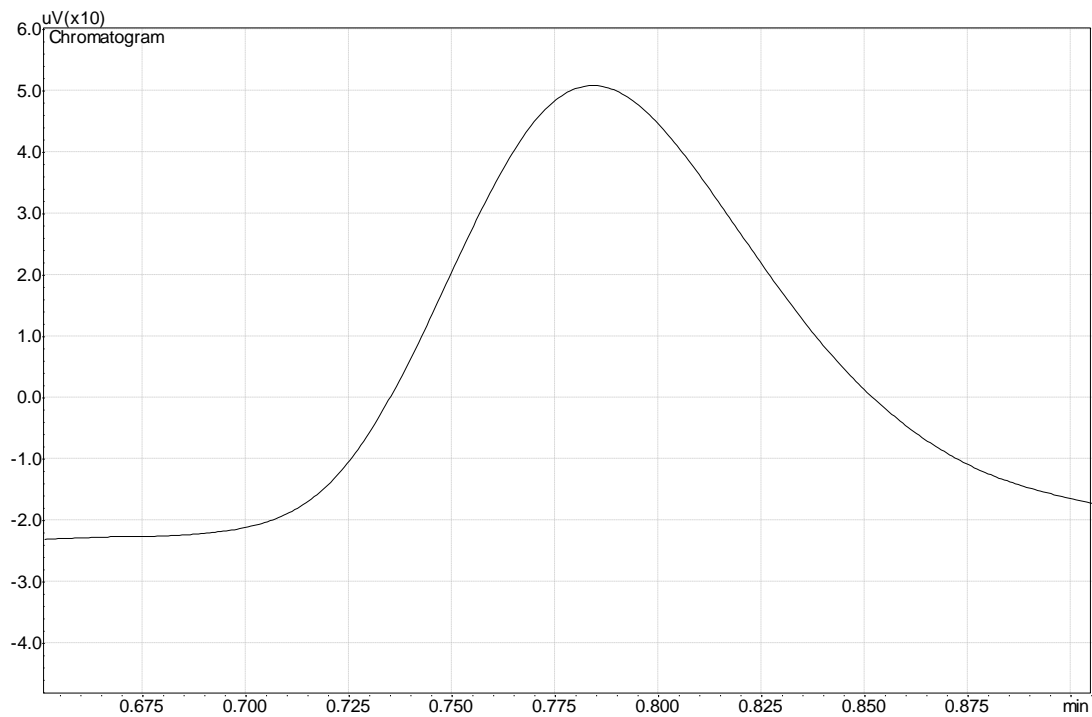
**Figure S1.** The transient current responses to on-off cycles of illumination on photocathodes under an applied potential of -0.4 V vs. Ag/AgCl in the PEC with Pt as the counter electrode,

operated in a 0.1 M  $\text{CH}_3\text{COONa}$  (pH 7.0) solution. The illumination was provided by a light emitting diode  $>400$  nm

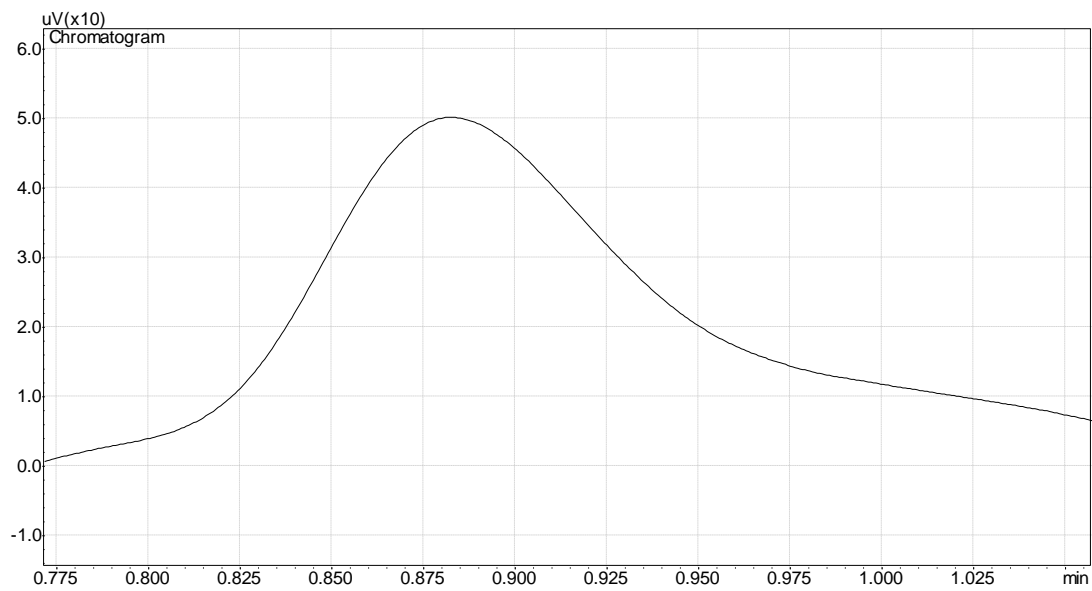


**Figure S2.** The photo-current decays for photocathodes under an applied potential of  $-0.4$  V vs. Ag/AgCl in the PEC with Pt as the counter electrode, operated in a 0.1 M  $\text{CH}_3\text{COONa}$  (pH 7.0) solution. The illumination was provided by a light emitting diode  $>400$  nm. The photocurrent decays were detected after three on-off cycles of illumination (figure S1).

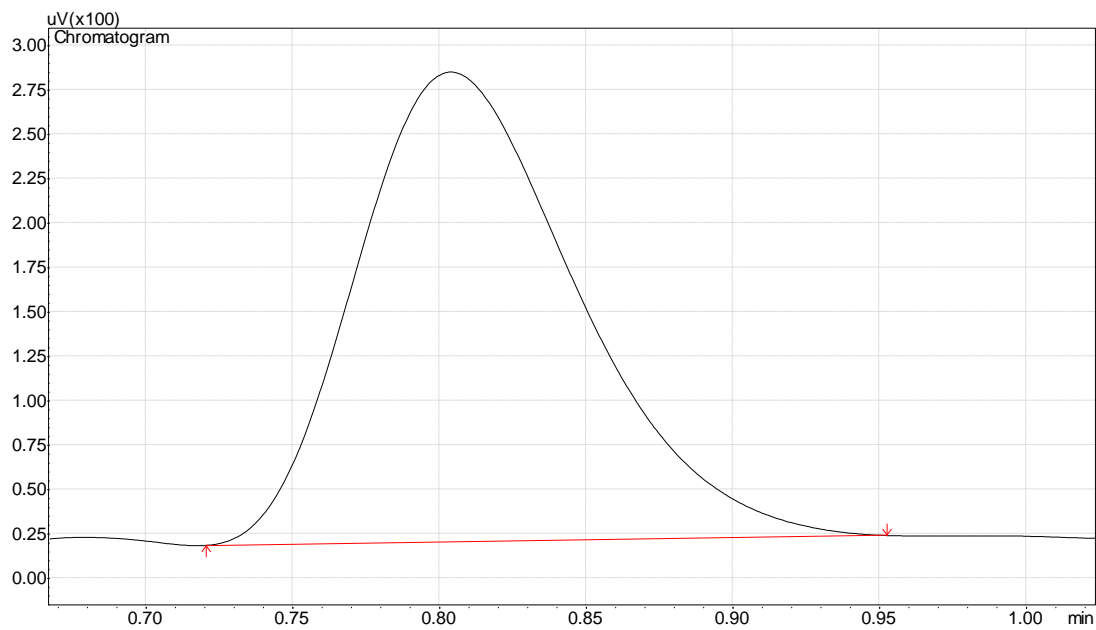
a)



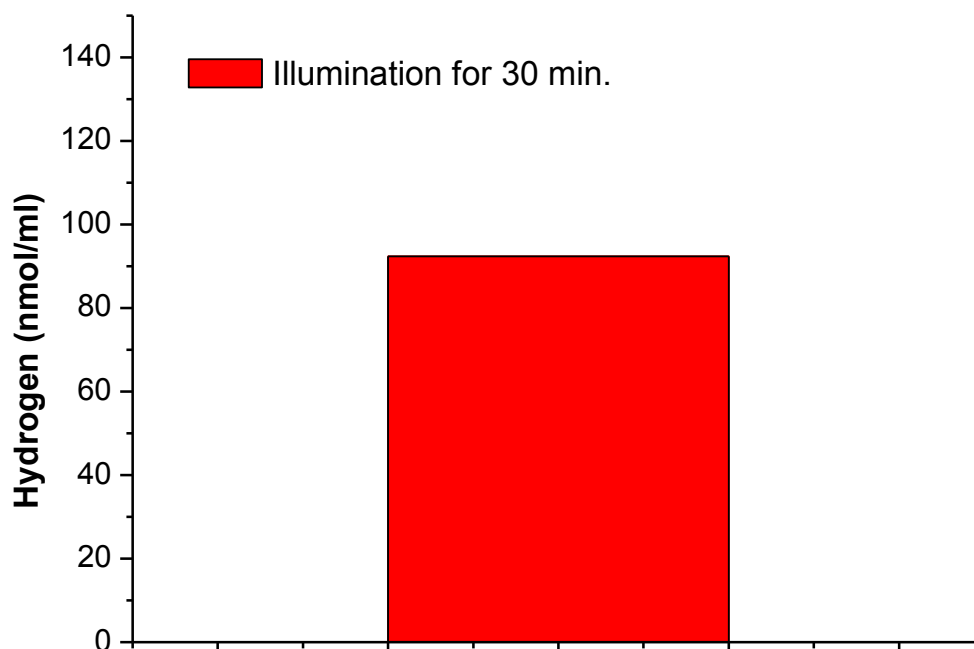
b)



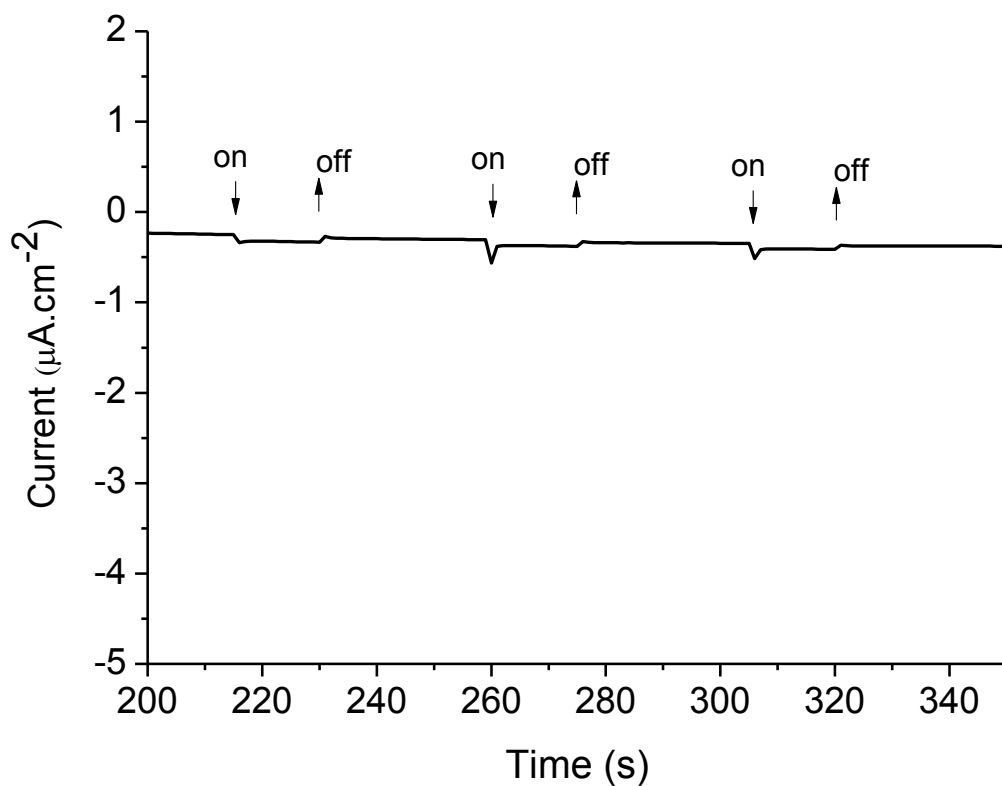
c)



**Figure S3.** GC data of a). Photoinduced hydrogen evolution from homogeneous systems containing **P1** ( $5 \times 10^{-5}$  M) + **Co1** ( $2 \times 10^{-4}$  M), in 1 mL solution contains 5% TEOA in 1:1 MeCN/H<sub>2</sub>O pH 7. b). 0.01 % hydrogen in nitrogen. c). 0.1 % hydrogen in nitrogen

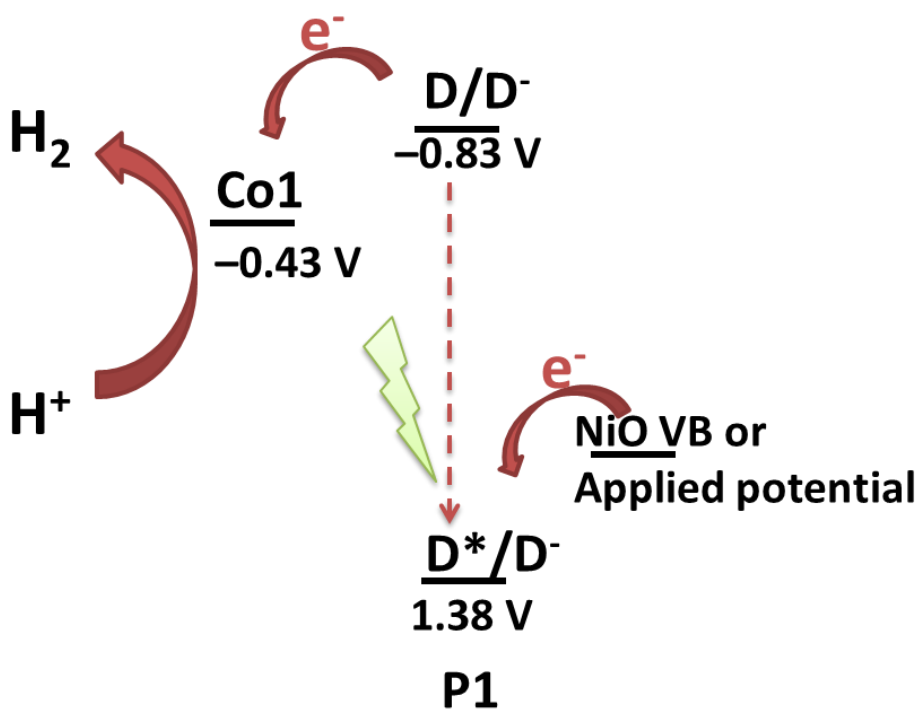


**Figure S4.** Hydrogen production in a PEC device, consisting of an photocathode NiO-P1-Co1, Pt counter electrode, and an aqueous electrolyte pH 7 buffer, under an applied potential of -0.4 V vs. Ag/AgCl, under the illumination for 30 min., measured by modified Clark electrode.

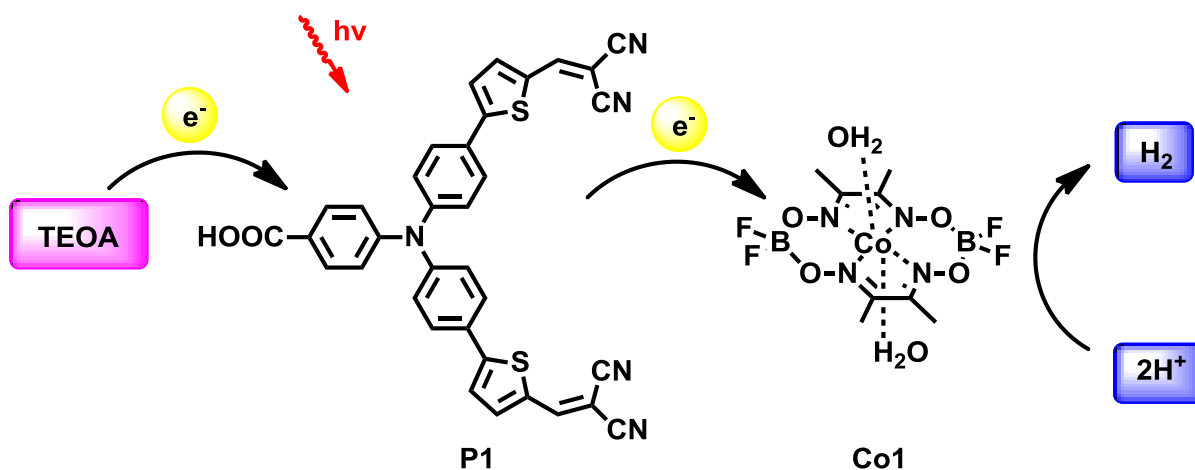


**Figure S5.** The transient current responses to on-off cycles of illumination on photocathode (NiO-P1-Co1) in the PEC with Pt as the counter electrode (two electrodes system, without any bias voltage), operated in a 0.1 M  $\text{CH}_3\text{COONa}$  (pH 7.0) solution. The illumination was provided by a light emitting diode  $>400$  nm





**Scheme S1.** Schematic energy diagram of a NiO-P1-Co1 electrode under visible light irradiation (V vs. NHE).



**Scheme S2.** Visible light-driven hydrogen generation using a three-component homogeneous system, consisting of **P1** as photosensitizer, **Co1** as proton reduction catalyst, and triethanolamine (TEOA) as sacrificial electron donor.