

Electronic Supplementary Information for  
Integrating Zeolite-Type Chalcogenide with Titanium Dioxide  
Nanowires for Enhanced Photoelectrochemical Activity

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## Experimental Sections

### 1. Materials Preparation

All of the reagents used were obtained from commercial supplies without further purification. Germanium (IV) oxide (=  $\text{GeO}_2$ , 99.999%, Acros Organics), sulfur powder (= S, 100 mesh, 99.5%, Alfa Aesar),  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (99.9%, Sigma Aldrich),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98% extrapure, Acros Organics),  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98%, Sigma-Aldrich), titanium (IV) iso-propoxide (Acros, 98+%) , N-(2-aminoethyl)-morpholine (= AEM,  $\text{C}_6\text{H}_{14}\text{N}_2\text{O}$ , 98+%, Alfa Aesar),

**Preparation of CPM-121- ZnGeGaS Powder:** CPM-121- ZnGeGaS powder sample was synthesized by a modified solvothermal method reported previously.<sup>1</sup> 120mg  $\text{GeO}_2$  (0.090 mg, 1.23 mmol; or  $\text{GeO}_2$ , 0.120 g, 1.14 mmol), 90mg  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 118 mg  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  and 200 mg sulfur (S, 0.220 g, 6.88 mmol) were added into 23 mL Teflon-lined stainless autoclave. Then 3 mL N-(2-aminoethyl) morpholine (AEM, 2.5 mL) was added and mixture were stirred overnight until no aggregates existed at the bottom of the autoclave. The vessel was then sealed and heated at 190 °C for 12 days. After cooling to room temperature, CPM-121-ZnGeGaS crystals was recovered and washed with methanol several times.

**Preparation of FTO-TiO<sub>2</sub>:** TiO<sub>2</sub> nanowire was grown on FTO following previous reported procedure.<sup>2</sup> 5 mL concentrated HCl (37% by volume) was mixed with 5 mL of deionized water in a beaker first. After stirring for 5 min, 167  $\mu\text{L}$  Ti(IV) iso-propoxide was added into the beaker. The mixture was stirred for another 3h before being moved into an autoclave. A clean FTO substrate was immersed into the autoclave with the conducting side facing down. The autoclave was put in a pre-heated 200 °C oven for 90 min. After the autoclave was taken out and cooled down to room temperature, FTO substrate was recovered and washed with deionized water and ethanol. The FTO substrate was then dried in an 80 °C oven first, followed by annealing in air at 400 °C for 1 h.

**Preparation of FTO- TiO<sub>2</sub>-CPM121:** 120mg  $\text{GeO}_2$  (0.090 mg, 1.23 mmol), 90mg  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 118 mg  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  and 200 mg sulfur (S, 0.220 g, 6.88 mmol) were added into 23 mL Teflon-lined stainless autoclave. Then 3 mL N-(2-aminoethyl) morpholine (AEM) was added and mixture were stirred overnight until no aggregates existed at the bottom of the autoclave. The as-obtained slurry was dropped onto TiO<sub>2</sub> side of FTO-TiO<sub>2</sub> by using a glass rod. FTO-TiO<sub>2</sub> was held vertically to remove extra slurry. The process was repeated for 3-5 times until the whole FTO-TiO<sub>2</sub> surface was covered by the slurry uniformly. The FTO-TiO<sub>2</sub> was then moved into an empty autoclave. The vessel was then sealed and heated at 190 °C for one week. After cooling to room temperature, the FTO was recovered from the autoclave and the yellow crystals was grown on the TiO<sub>2</sub> surface.

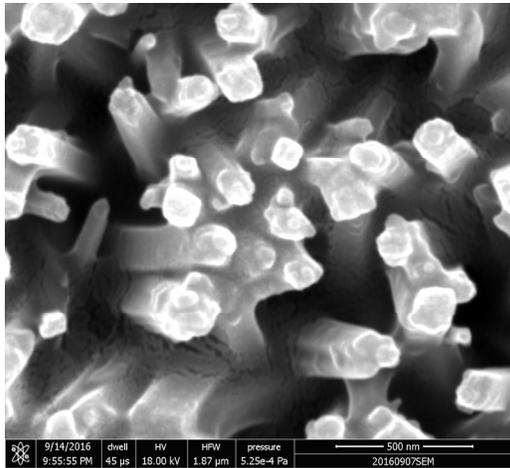
## 2. Materials Characterization

Powder X-ray diffraction data were collected using a Bruker D8 Advance powder diffractometer operating at 40 kV, 40mA with Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation. UV-VIS adsorption spectra were recorded on a SHIMADZU UV-3150 UV-VIS Scanning Spectrophotometer. The morphology and semi-quantitative elemental analyses of different samples were characterized by using Nova Nano-SEM450 (Schottky field emission scanning electron microscope) equipped with Oxford Instruments Aztec energy dispersive spectroscopy detector. Pt/Pd as conducting metal was sputtered onto the sample before SEM analysis. Data acquisition was performed with an accelerating voltage of 15-20 kV and 30 s accumulation time.

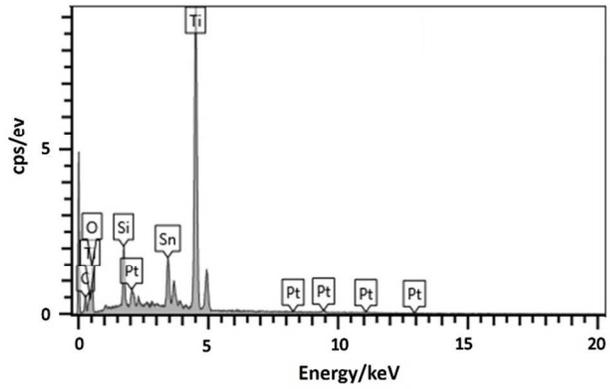
## 3. Photoelectrochemical measurement

Powder CPM-121 was loaded onto FTO current collector by electrophoresis. 20mg samples and 3mg  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were added into 40mL isopropanol and kept under stir for 3 days, followed by 1h sonication before electrophoresis. FTO electrode was connected to the negative electrode while Pt wire was used as positive. 50 V DC voltage was applied for 30 min to deposit the active materials on the FTO electrode. Photoelectrochemical measurements were carried out using a Solartron 1287 electrochemical interface analysis instrument operated with the CorrWare program in a standard three-electrode configuration with the samples used as working electrode, a Pt foil as counter electrode, and an Ag/AgCl electrode as the reference electrode. 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution was used as the electrolyte. A 150 W Xenon lamp (Newport, 69907) coupled with a 420 nm cut-on filter (Newport) was applied as the visible light source. The gaseous product on the cathode was collected by electrolyte displacement and analyzed by gas chromatography (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD).

The electrochemical impedance spectroscopy (EIS) was carried out using Solartron 1260 impedance/gain-phase analyzer connected to a Solartron 1287 electrochemistry interface. Zplot 2.6b was used as the control software and ZView 2.6b was used as the analysis software. A typical measurement was conducted over a frequency range of  $10^{-2}$  to  $5 \times 10^4$  Hz with an AC voltage amplitude of 50 mV. A DC bias equal to open circuit potential was applied to each different electrode.



(A)



(B)

Figure S1 (A) SEM image and (B) EDX spectra of  $\text{TiO}_2$  nanowires grown vertically on FTO, Pt signals came from Pt sputtering during sample preparation

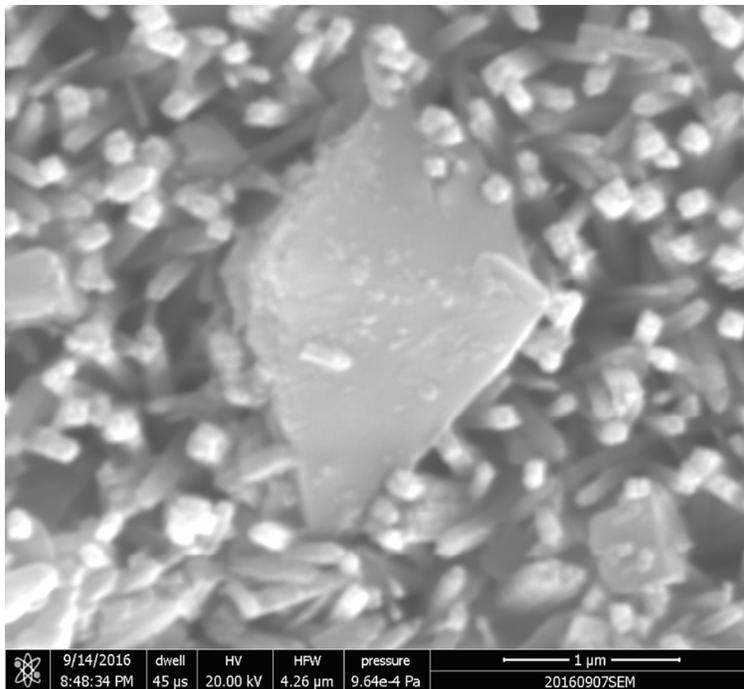
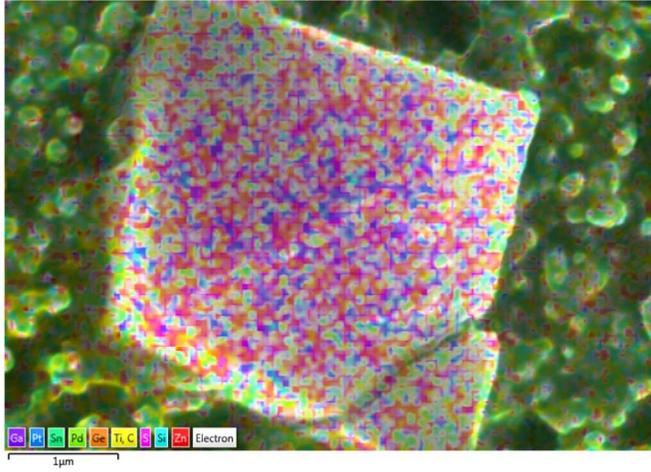
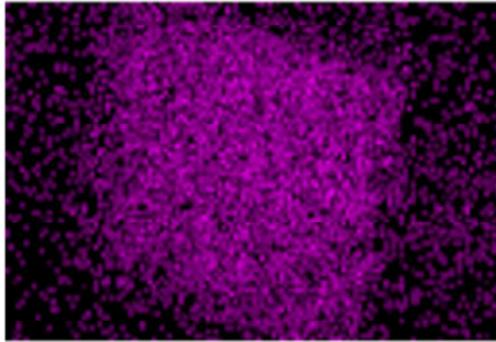


Figure S2. SEM image of FTO-  $\text{TiO}_2$ -CPM121.

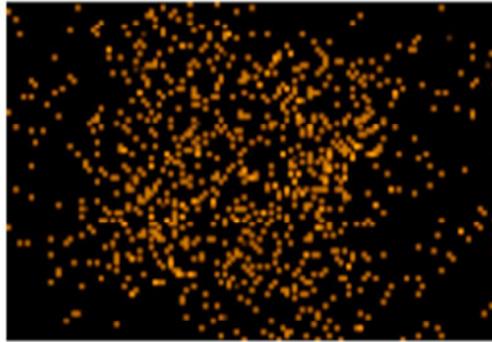
EDS Layered Image 10



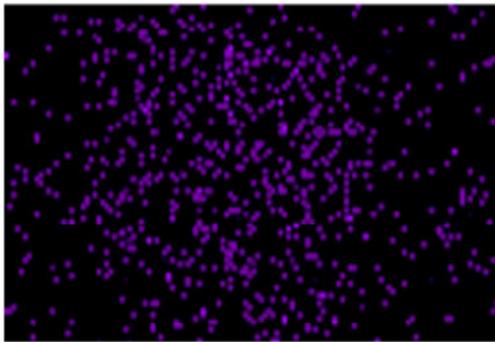
S Kα1



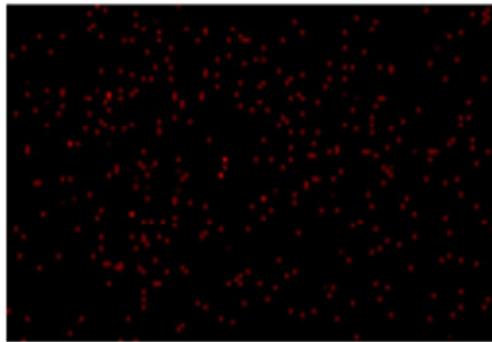
Ge Kα1



Ga Kα1



Zn Kα1



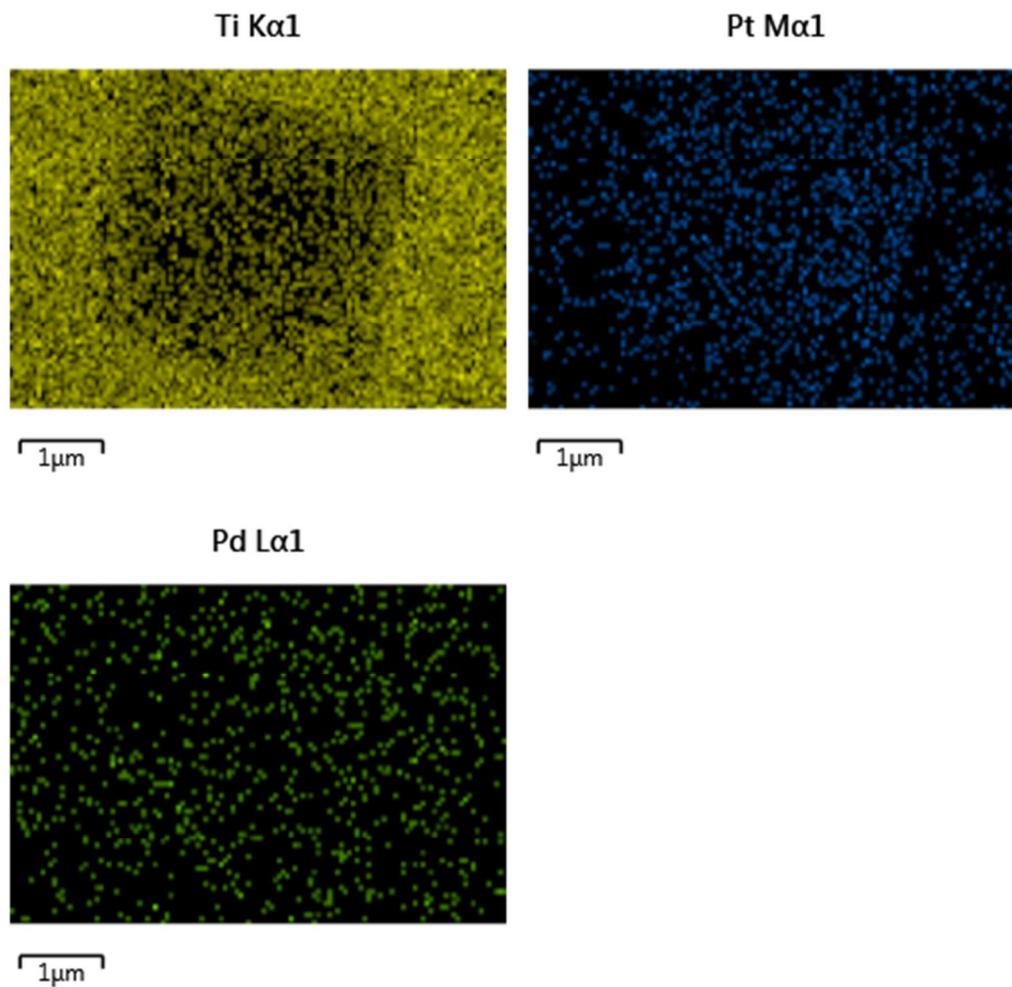


Figure S3. Elemental mapping of FTO- TiO<sub>2</sub>-CPM121, Pt and Pd signals came from sputtering during sample preparation

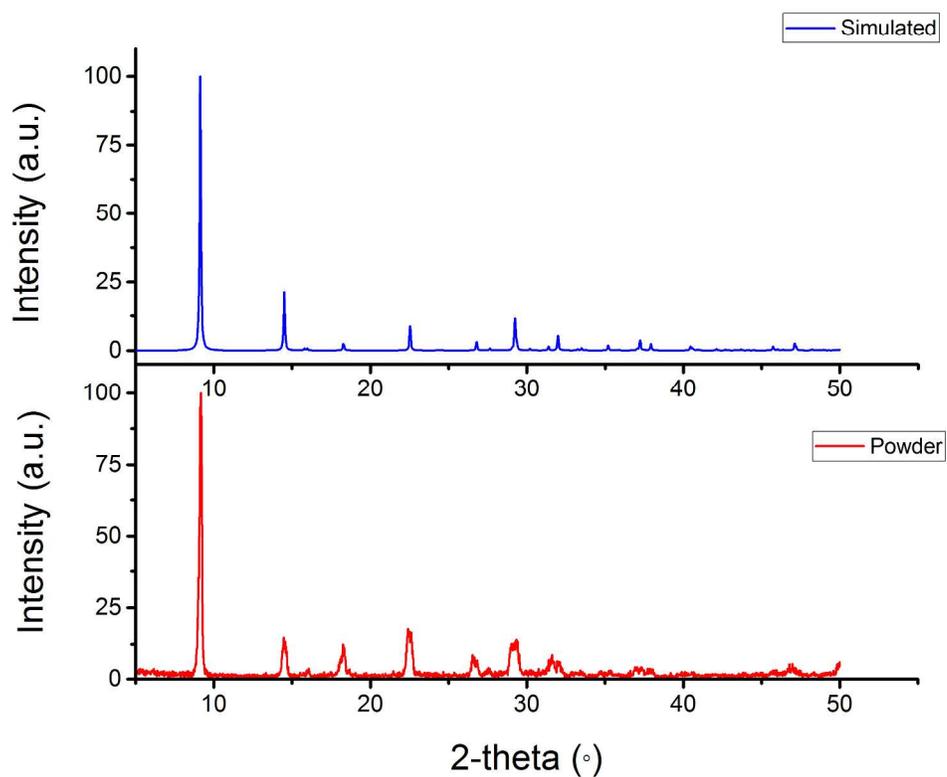


Figure S4. PXRD of CPM-121 powder and the simulated pattern from single-crystal data.

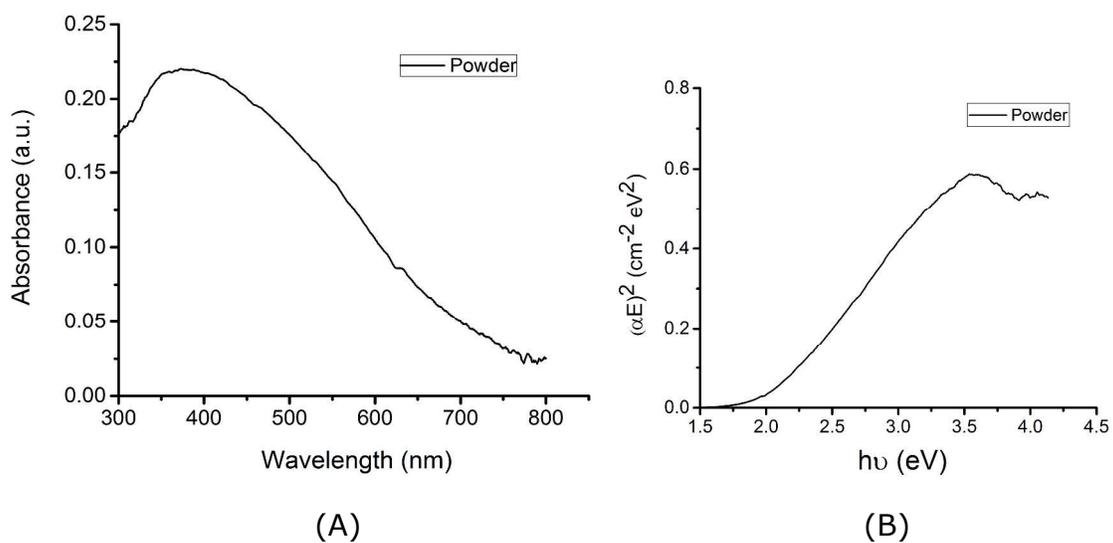


Figure S5. (A) UV-vis spectrum and (B) tauc plot of CPM-121 powder.

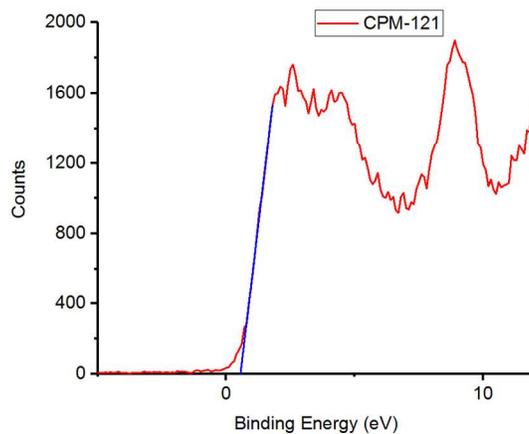


Figure S6. XPS-VB spectra of CPM-121

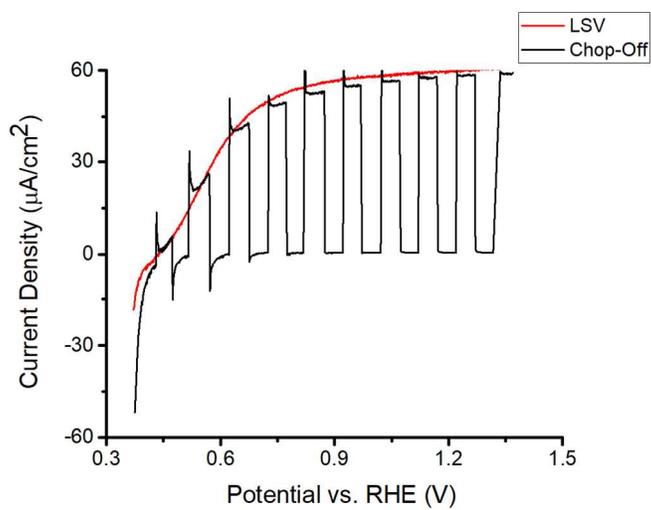


Figure S7. Current-potential plot for FTO- TiO<sub>2</sub>-CPM121 on continuous and chop-off illumination.

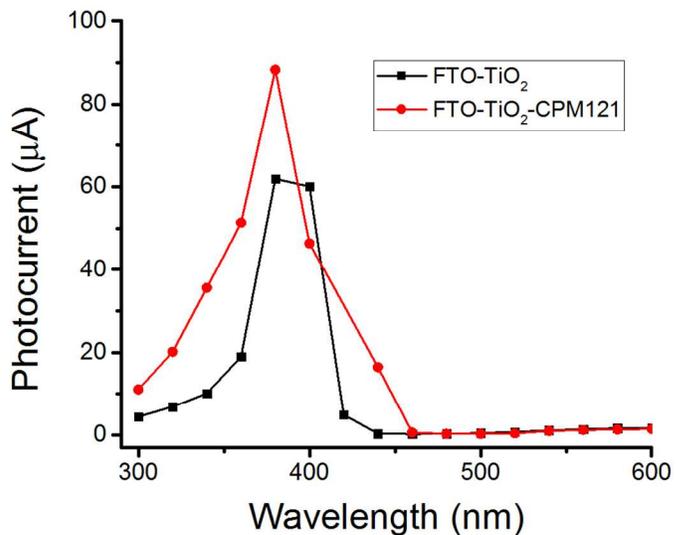


Figure S8 : Action spectra of photocurrents from FTO-TiO<sub>2</sub> and FTO-TiO<sub>2</sub>-CPM121

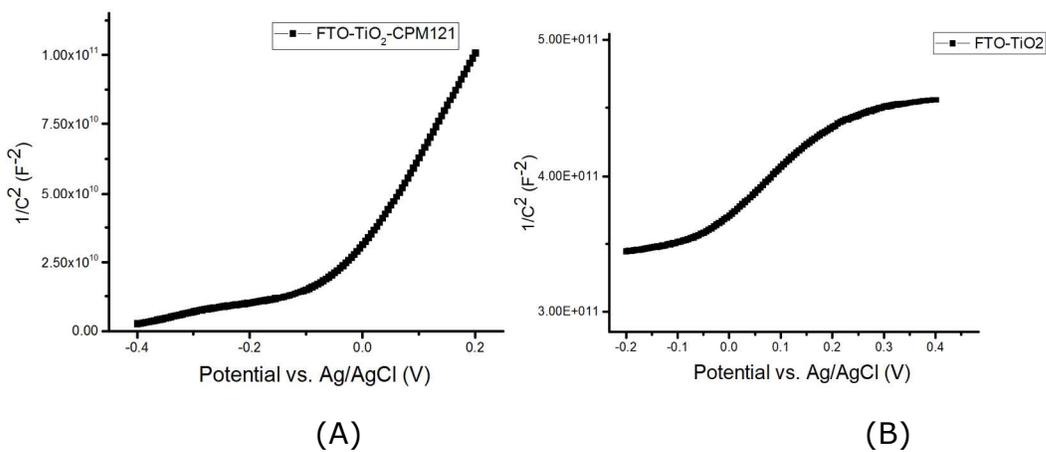
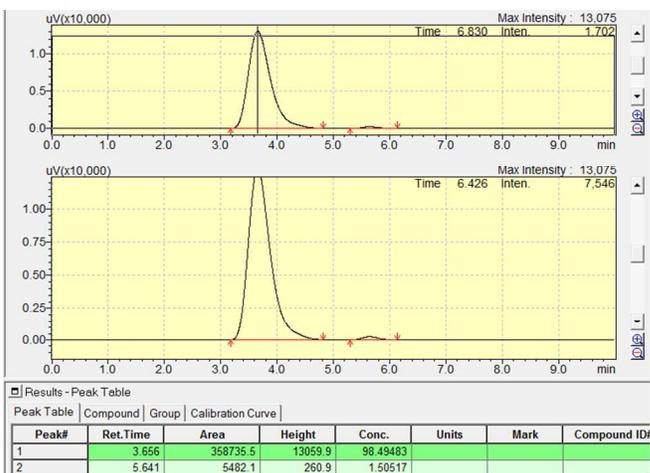
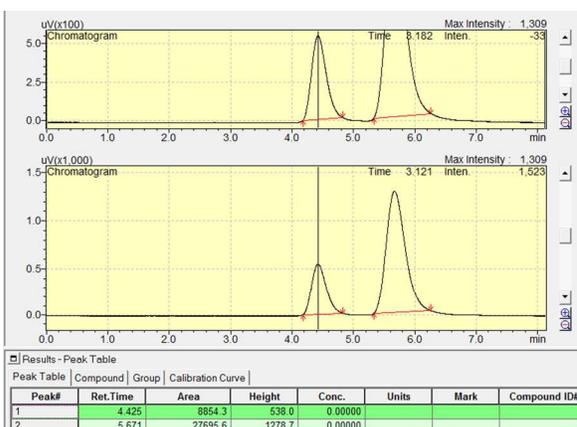


Figure S9 Mott-Schottky plot of (A) FTO-TiO<sub>2</sub>-CPM121 and (B) FTO-TiO<sub>2</sub>



(A)



(B)

Figure S10. A) GC profile of Gas Product collected on the cathode side of the reactor B) GC profile of air as reference.

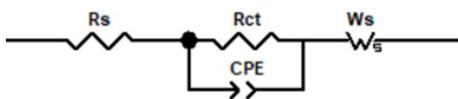


Figure S11. Equivalent circuit model for Electrochemical Impedance Spectra (EIS) analysis.

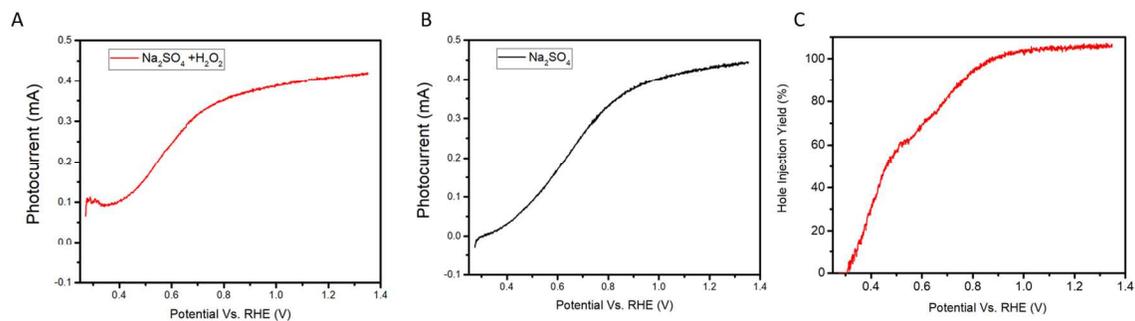


Figure S12: photocurrent of FTO-TiO<sub>2</sub>-CPM121 under AM 1.5 illumination in (A) the presence and (B) the absence of H<sub>2</sub>O<sub>2</sub>, (C) hole injection yield of FTO-TiO<sub>2</sub>-CPM121

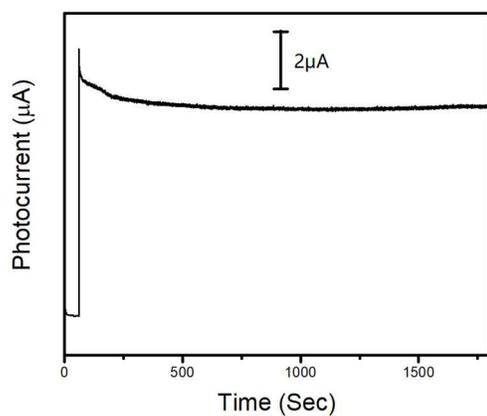


Figure S13. Stability test of FTO-TiO<sub>2</sub>-CPM121 under visible light illumination (455 nm cut-off filter)

#### References.

- S1. Lin, Q.; Bu, X.; Mao, C.; Zhao, X.; Sasan, K.; Feng, P., Mimicking High-Silica Zeolites: Highly Stable Germanium-and Tin-Rich Zeolite-Type Chalcogenides. *J. Am. Chem. Soc.* **2015**, *137*, 6184-6187
- S2. Liu, B.; Yang, P., Photoelectrochemical Properties of TiO<sub>2</sub> Nanowire Arrays: A Study of the Dependence on Length and Atomic Layer Deposition Coating. *ACS Nano* **2012**, *6* (6), 5060-5069.