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# Supporting Information

# Sn-doped Hematite Film as Photoanode for Efficient Photoelectrochemical Water Oxidation

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## 1. Experimental

All chemical compounds employed in this work were purchased from Aladdin. $FeCl_3 \cdot 6H_2O$ (99%), NaF (98%), KCl (99.5%), $H_2O_2$ (30%), $SnCl_2 \cdot 2H_2O$ (98%) and NaOH (96%) were used as received without further purification. DI water was used throughout the sample preparation and measurement. The FTO glass was purchased from Ao Pi Wei Te Company (Dalian, China) and used as received.

The detailed procedure for modification of samples with $Co^{2+}$ is as follows: The samples were dipped in the 0.1 M $Co(NO_3)_2 \cdot 6H_2O$ aqueous solution for 1 min. After that, the samples were taken out and dried at room temperature for 1 min., and then followed by washing with DI water.

The conversion efficiency is estimated using the following equation: $\eta = \frac{I(1.23 - V)}{J_{light}} \times 100\%$,[1-5] where V is the bias potential vs. RHE, I is the photocurrent density at the measured potential, and $J_{light}$ is the power density of incident light.

The morphology of the hematite films were characterized by using a field-emission scanning electron microscope (Hitachi S-4800) operated at an accelerating voltage of 5 kV. X-ray diffraction patterns (XRD) were recorded on a D/max-2400 (Rigaku) instrument using Cu Kα radiation ($\lambda$ = 1.5406 Å) between 20° to 70° at a scanning rate of 0.067°/s. Raman spectra were recorded at a JY-HR800 Micro-Raman, using a 532 nm wavelength YAG laser with a laser spot diameter of about 600 nm. The elements composition was determined by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). Photoluminescence and Time-Correlated Single Photon Counting were tested in FLS920 (Edinburgh Instruments). UV-visible diffusion reflectance spectra were measured on a UV-2550 (Shimadzu) spectrometer by using bare FTO as reference. Photoelectrochemical measurements were tested using a three-electrode configuration with the hematite films as the working photoelectrode, saturated calomel electrode (SCE) as the reference electrode, and platinum foil as the counter electrode in 1 M NaOH. Sunlight was simulated with a 300 W xenon lamp and an AM1.5G filter (HSX-F300, Beijing NBeT Technology Co., Ltd). The light intensity was set to 100 $mW \cdot cm^{-2}$ using a calibrated crystalline silicon solar cell. Photocurrent response and electrochemical impedance spectroscopy (EIS) were recorded using a CHI-660E potentiostat, with the data fit to an equivalent circuit model using ZView software. The superimposed alternating current (AC) signal was maintained at 5 mV, while the frequency was scanned between 100 kHz and 0.1 Hz at potentials between 0.7 and 1.3 V versus RHE in the dark and under illumination in an electrolyte of 1 M NaOH, with Pt as the counter electrode. The capacitance was extracted from the EIS spectra by use of an equivalent circuit Rs(CPE-Rp), where Rs is the ohmic contribution, CPE is the constant phase element that takes into account non-idealities in the capacitance of the Helmholtz layer, and Rp is the charge-transfer resistance. IPCE were measured using light from a 300 W xenon lamp that was focused by a parabolic reflector and passed through a monochromator, at 1.2 V bias versus RHE. Samples were measured using a hematite film as the working photoelectrode and platinum foil as the counter electrode in 1 M NaOH.

## 2. Raman spectra

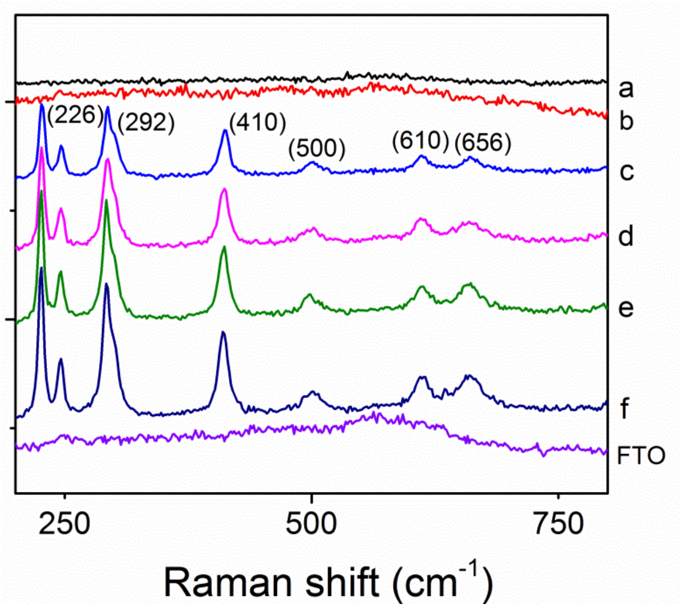
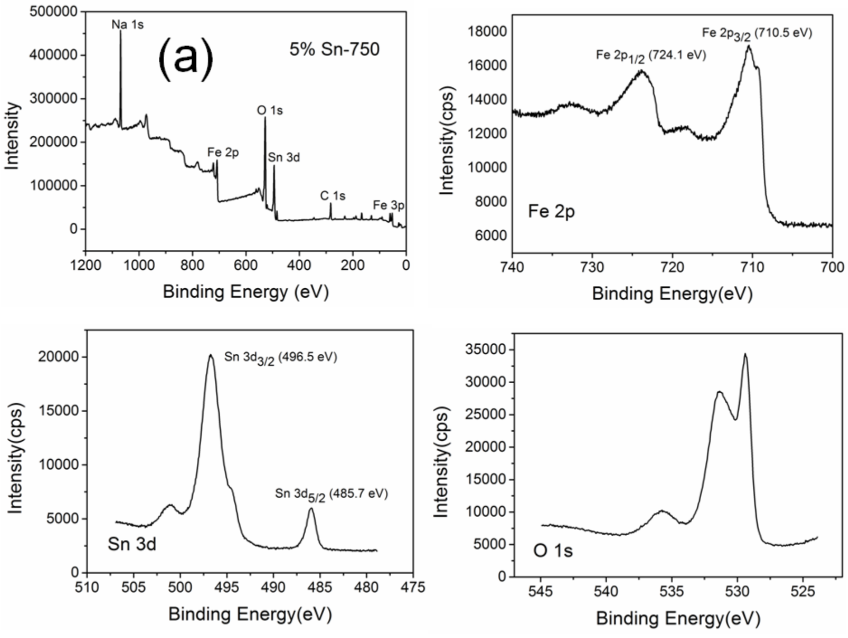


**Fig. S1** Raman spectra of the samples: a) and b) 0% and 5% Sn doped samples without thermal annealing, c), d), e) and f) 0%, 2%, 5%, 10% Sn doped samples after annealing at 750 ºC for 30 min.

## 3. XPS spectra



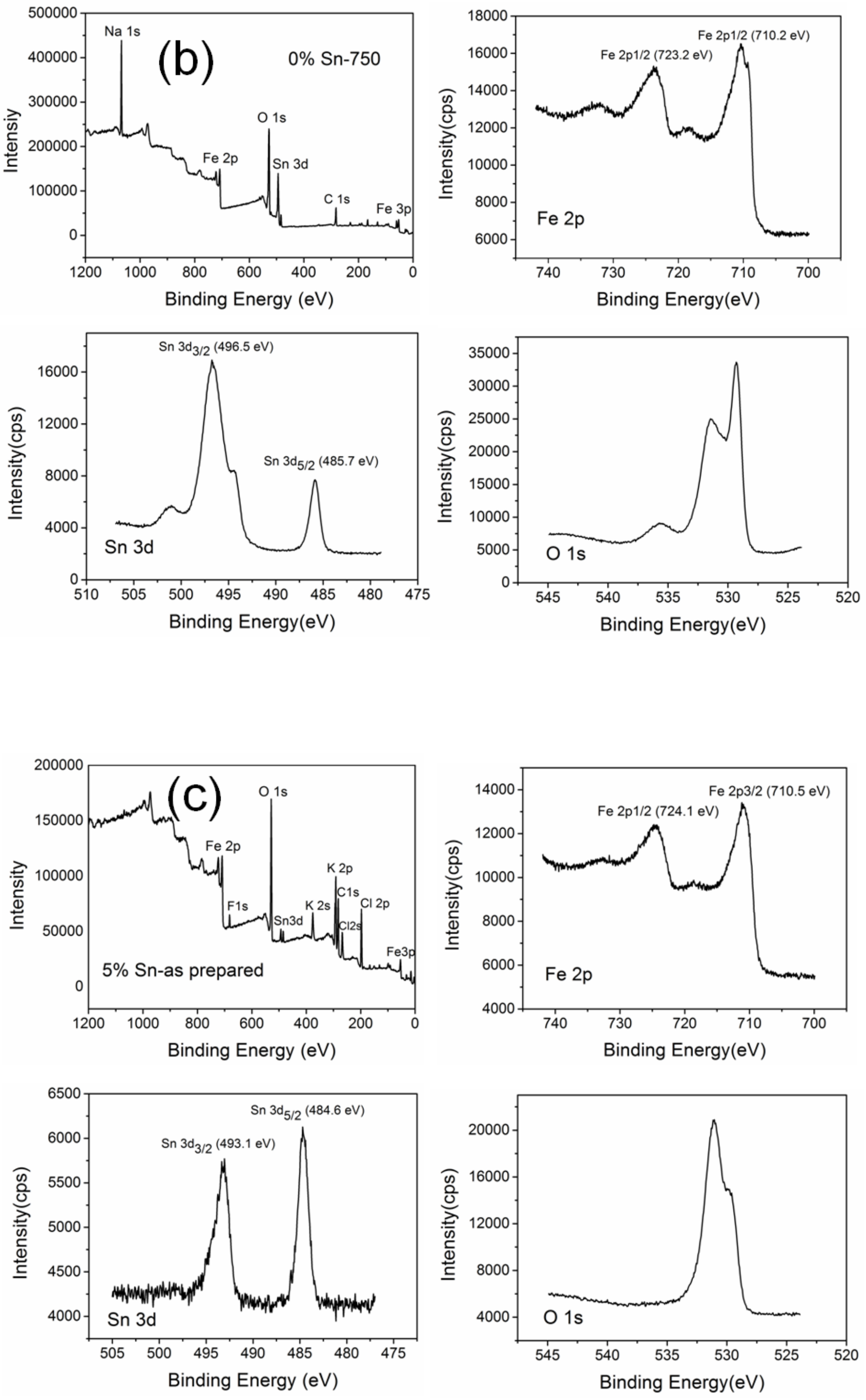


**Fig. S2** XPS data of samples, a) 5% Sn-750 ºC; b) 0% -750 ºC; c) 5% Sn as prepared.

## 4. Optical spectra

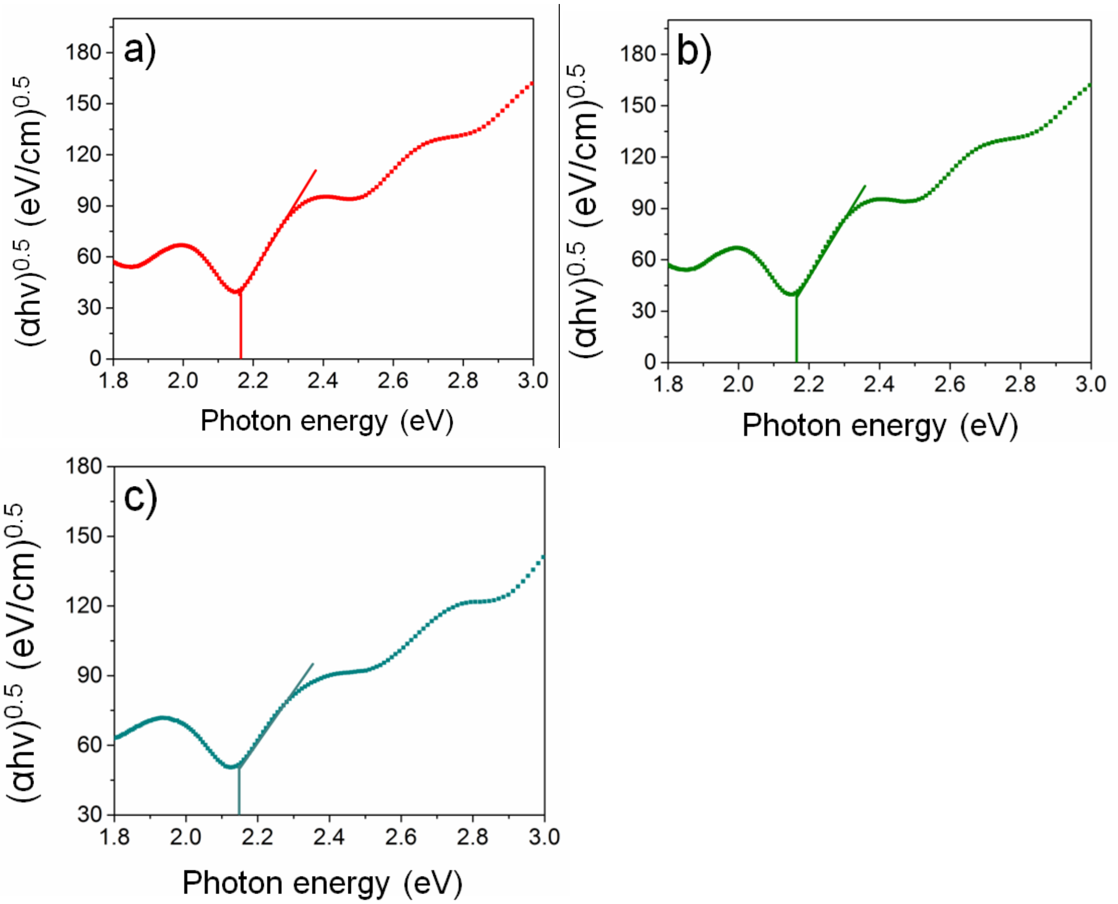


**Fig. S3** Optical spectra of 5% Sn-750, 0% Sn-750 and 5% Sn-as prepared samples.

## 5. Photoluminescence spectra

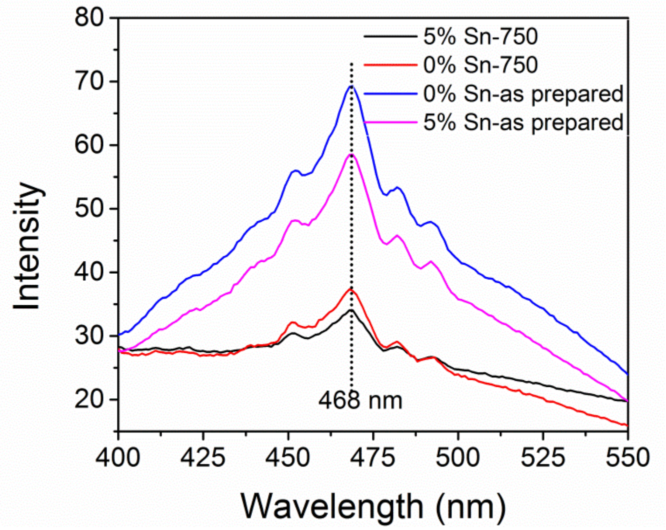


**Fig. S4** Photoluminescence spectra of samples, with excitation wavelength of 360 nm.

## 6. Time-Correlated Single Photon Counting

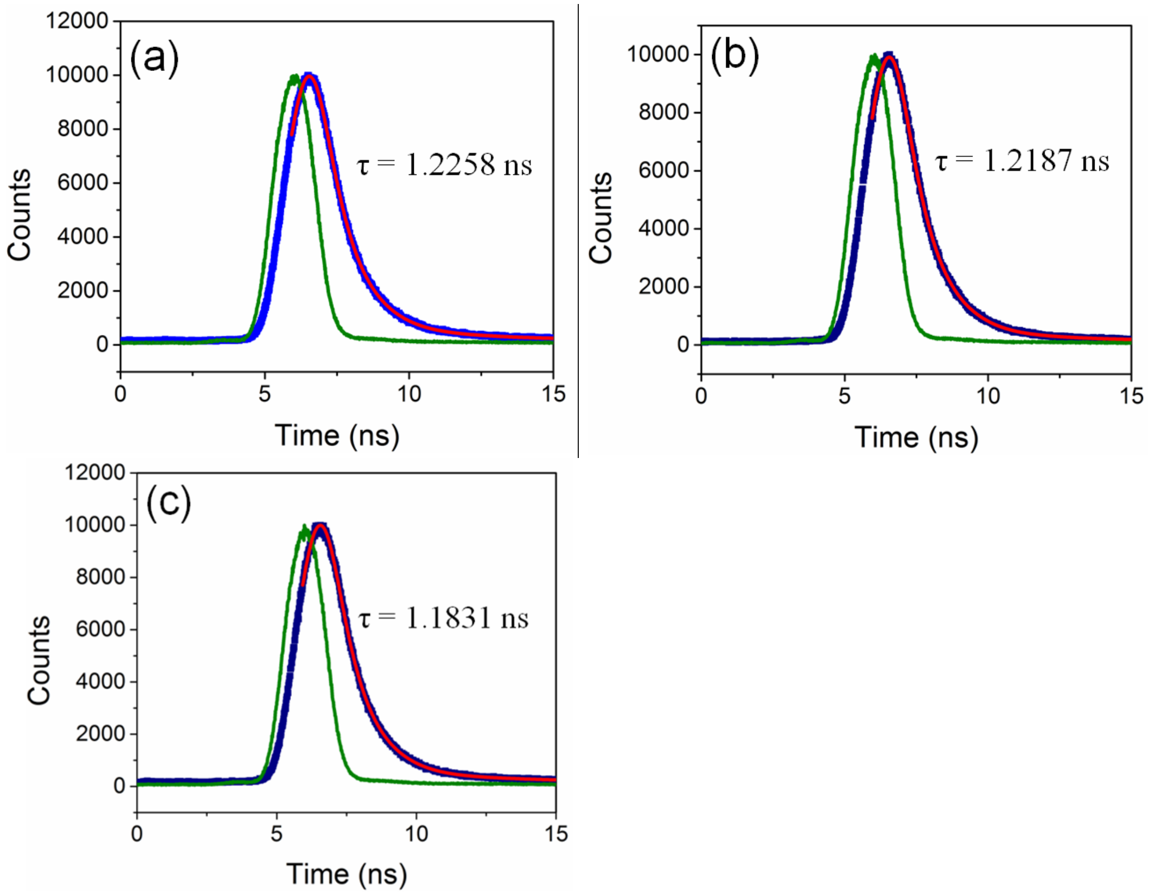


**Fig. S5** Time-Correlated Single Photon Counting results (blue line) for the samples of 5% Sn-750 (a), 0% Sn-750 (b) and 5% Sn-as prepared (c) at 298 K. Excitation: 360 nm, emission: 468 nm. The red line is the best fit results. Green line is the IRF curve.

## 7. Photocurrent response of the samples

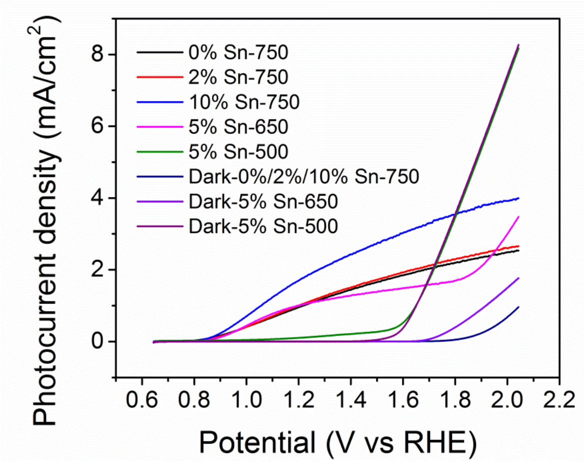


**Fig. S6** Photocurrent of the samples in 1 M NaOH, under illumination of AM 1.5G (100 mW·cm$^{-2}$).

## 8. Influence of deposition time and heating rate to the photocurrent of the samples

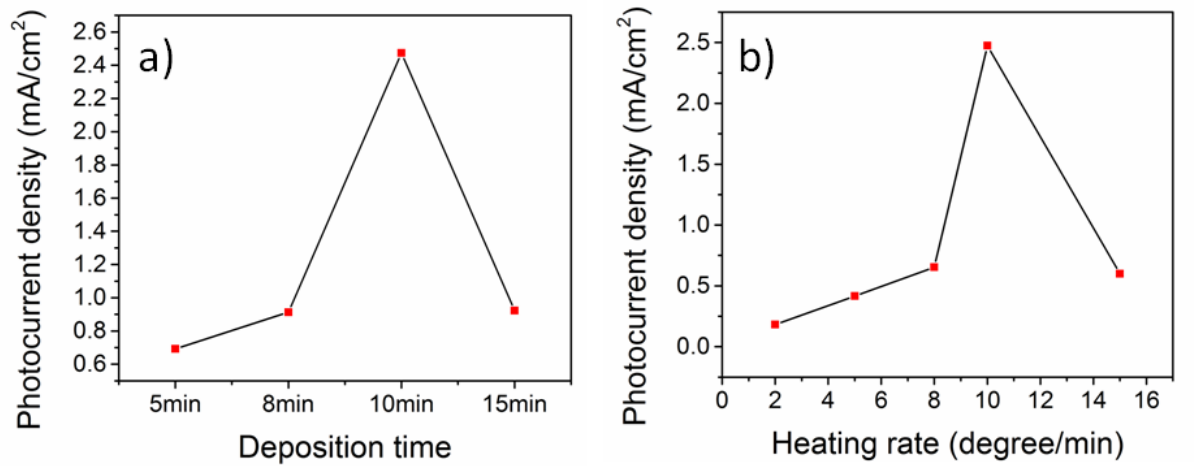


**Fig. S7** a) Photocurrent of the 5% Sn doped sample with different electrochemical deposition time after being annealed at 750 ºC for 30 min. with a heating rate of 10 ºC/min.; b) Photocurrent of the 5% Sn doped, 10 min. electrochemical deposited sample after being annealed at 750 ºC for 30 min. with different heating rate. The photocurrent was recorded at bias of 1.24 V vs RHE in 1.0 M NaOH, under illumination of AM 1.5 G, 100 mW·cm$^{-2}$.

## 9. Photocurrent response under chopped light.

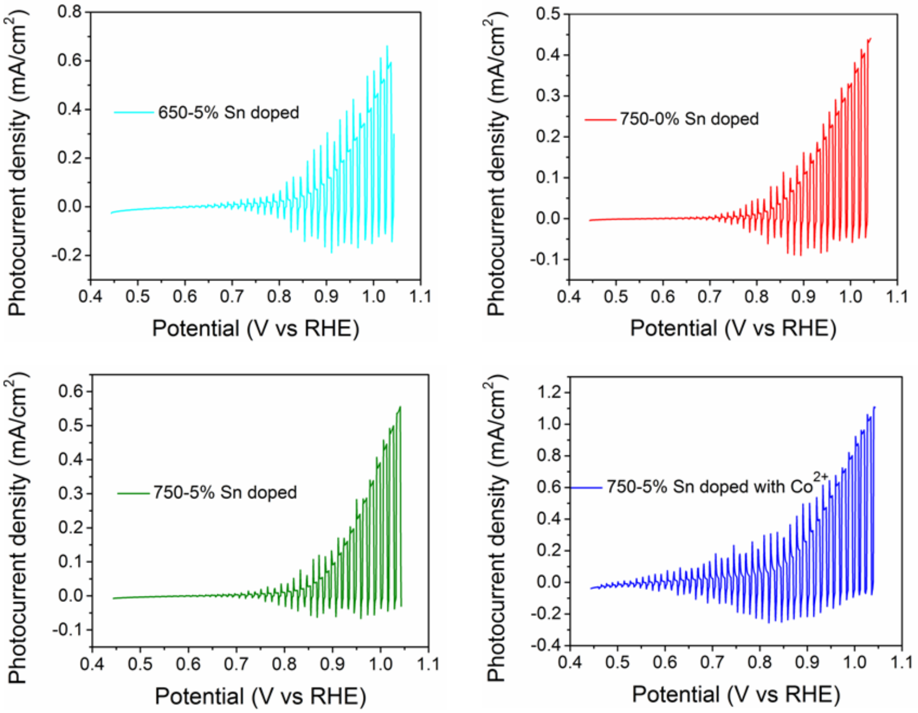


**Fig. S8** Photocurrent response of the samples under chopped light in 1 M NaOH, with illumination of AM 1.5G, 100 mW·cm$^{-2}$.

References:

1. Yang Hou, Fan Zuo, Alex Dagg, and Pingyun Feng, *Angew. Chem. Int. Ed.* **2013**, *52*, 1248-1253.
2. Damon A. Wheeler, Gongming Wang, Yichuan Ling, Yat Li and Jin Z. Zhang, *Energy Environ. Sci.*, **2012**, *5*, 6682–6702.
3. Yang Hou, Fan Zuo, Alex Dagg, and Pingyun Feng, *Nano Lett*. **2012**, *12*, 6464−6473.
4. Gurudayal, Sing Yang Chiam, Mulmudi Hemant Kumar, Prince Saurabh Bassi, Hwee Leng Seng, James Barber, and Lydia Helena Wong, *ACS Appl. Mater. Interfaces* **2014**, *6*, 5852−5859.
5. Z. Chen, T. F. Jaramillo et al, *J. Mater. Res*., **2010**, *25*, 3−16