

## Electronic Supplementary Information

### **Concentrated solar light for rapid crystallization of nanomaterials and extreme enhancement of photoelectrochemical performance**

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## Experimental Section

**Chemicals and materials.** A Fresnel lens with diameter of 12 inch was purchased from Edmund Optics. A 0.1 mm thick titanium foil (99.6%, Jinjia Metal, China) was cut into pieces of  $40 \times 10$  mm<sup>2</sup>. The fluoride-doped tin oxide (FTO) glass, purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd, China. Copper foil with thickness of 1 mm was purchased from Good Fellow Cambridge Ltd. Ethylene glycol (EG), ammonia fluoride (NH<sub>4</sub>F), ethanol, Iron (III) chloride (FeCl<sub>3</sub>), urea, isopropyl titanate, hydrochloric (HCl), sodium hydroxide (NaOH), were purchased from Macklin Chemical and used as received. All aqueous solutions were prepared using deionized water (DI) with a resistivity of 18.2 MΩ cm.

**Preparation of TiO<sub>2</sub> NTs.** The TiO<sub>2</sub> NTs were fabricated by a two-step anodization process. Prior to anodization, the Ti foils were first degreased by sonicating in ethanol and DI water, followed by drying in pure nitrogen stream. The anodization was carried out using a conventional two-electrode system with the Ti foil as an anode and a Pt foil as a cathode respectively. All electrolytes consisted of 0.5 wt% NH<sub>4</sub>F in EG solution with 2 vol% water. All the anodization was carried out at room temperature. In the first-step anodization, the Ti foil was anodized at 60 V for 30 min, and then the as-grown nanotube layer was ultrasonically removed in deionized water. The same Ti foil then underwent the second anodization sequentially at 20 V, 25 V, and 30 V for 30 min, respectively. After the two-step anodization, the prepared TiO<sub>2</sub> NTs samples were cleaned with DI water and dried off with nitrogen gas. Finally, the as-anodized TiO<sub>2</sub> NTs were annealed in the concentrated solar light (CSL) system for 30 min.

**Preparation of TiO<sub>2</sub> NWs.** The synthesis of FTO-TiO<sub>2</sub> NWs was carried out in a 25 mL Teflon-lined stainless-steel autoclave. In a typical procedure, 10 mL HCl were dissolved in 10 mL DI water.

After stirring for 10 min, 0.5 mL of isopropyl titanate were added into the mixture. The mixture was transferred into the Teflon-lined stainless-steel autoclave and maintained at 150 °C for 12 h. Finally, the autoclave was cooled down to room temperature. The FTO glass was covered with white TiO<sub>2</sub> nanowires and washed with DI water for several times. The as-prepared TiO<sub>2</sub> nanowires were annealed in the CSL system for 30 min.

**Preparation of Fe<sub>2</sub>O<sub>3</sub> NWs.** The substrates of FTO (1 cm×4 cm) were firstly cleaned in actone, ethanol and deionized water for 20 min respectively. Typically, 0.1 M FeCl<sub>3</sub> and 0.15 M urea were dissolved in a 12 mL solution. And then transferred it into a Teflon-lined stainless autoclave (25 mL), a piece of cleaned FTO was immersed into the solution. Then the autoclave was sealed and maintained at 100 °C for 4 h in an electric oven. When the autoclave cooled down naturally, the resulting Fe<sub>2</sub>O<sub>3</sub>/FTO was taken out and washed with ultrapure water. Finally, the Fe<sub>2</sub>O<sub>3</sub>/FTO was annealed in the CSL system for 30 min.

**Preparation of CuO NWs.** The Cu foil was anodized in an alkali solution (3 M NaOH) for 30 min under 10 mA cm<sup>-2</sup> to form Cu(OH)<sub>2</sub> NWs. The temperature of the electrochemical cells was maintained at 25 °C for all experiments. The as-anodized NWs were annealed in the CSL system for 30 min to converted Cu(OH)<sub>2</sub> NWs to CuO NWs.

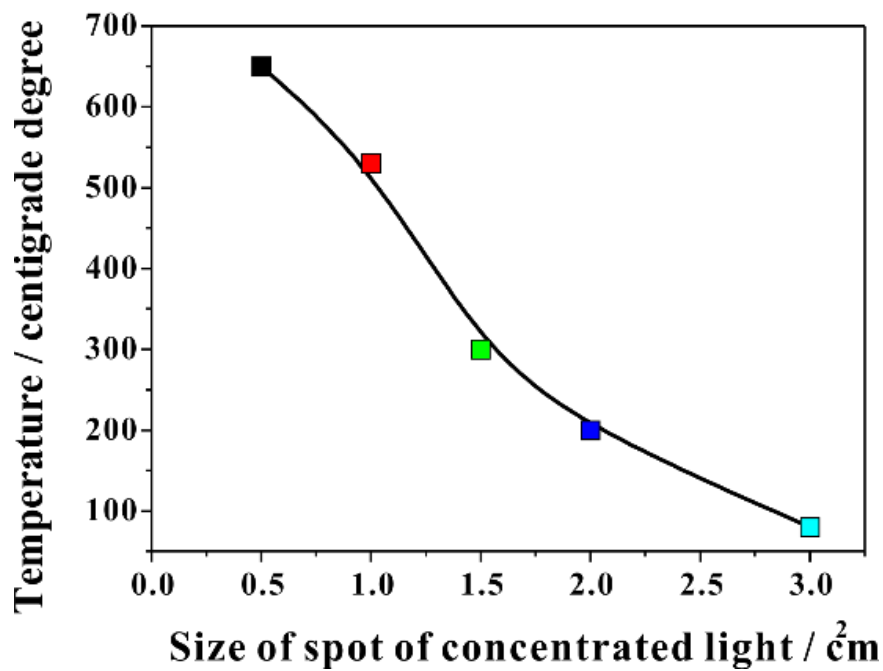
**Materials Characterization.** The morphologies of samples were characterized by scanning electron microscopy (SEM, S4800, Hitachi), and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM 2100). The crystalline structure of the samples was analyzed by X-ray diffraction (XRD) (Bruker D8 Discover diffractometer, using Cu K $\alpha$  radiation (1.540598 Å)). The Raman spectra were measured through DXR Raman Microscope (ThermoFisher Scientific). The diffuse reflectance UV-vis adsorption spectra were recorded on a spectrophotometer (Shimadzu, UV

3600), with fine BaSO<sub>4</sub> powder as reference.

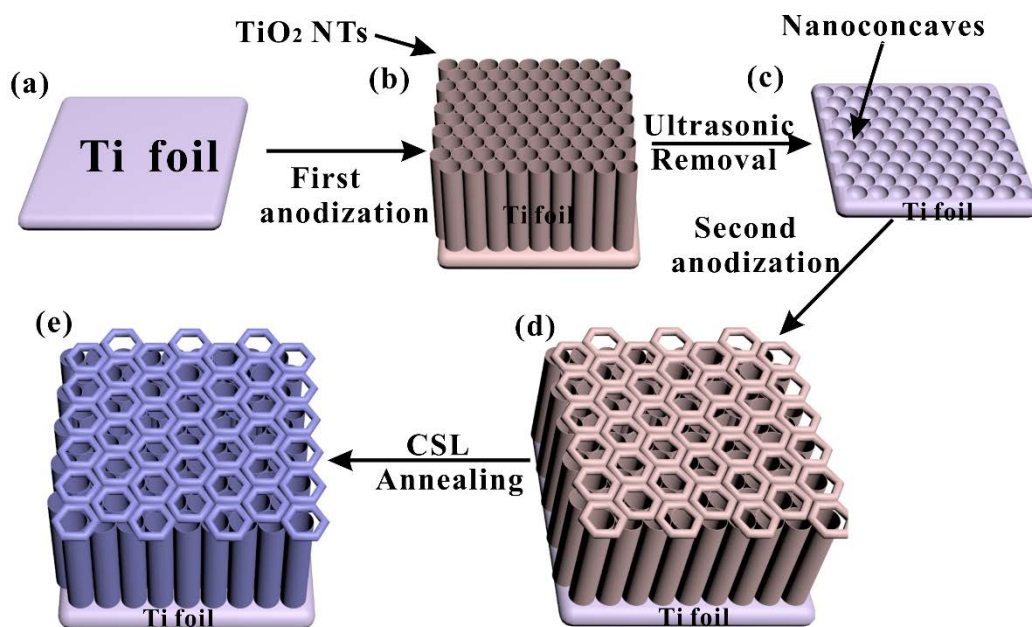
**Photoelectrochemical (PEC) measurements.** All the PEC measurements were performed with CHI 660E electrochemical working station in a three-electrode system with photoelectrodes as working electrode, a platinum foil as the counter electrode, and Ag/AgCl with saturated KCl solution as the reference electrode. The supporting electrolyte was a 1 M NaOH solution. The potential of the photoelectrodes were controlled by a potentiostat and were reported against the reversible hydrogen electrode (RHE) following the equation below:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}} \text{ with}$$
$$E^{\circ}_{\text{Ag/AgCl}} = 0.1976 \text{ V at } 25 \text{ }^{\circ}\text{C} \quad (1)$$

The scan rate for the linear sweep voltammetry (LSV) was 5 mV s<sup>-1</sup>. The photocurrent was measured under an irradiation from a 300 W Xe lamp (PLS-SXE300, PE300BF). The intensity of the light source was calibrated with a Si diode (Model 818, Newport) to simulate AM 1.5 illumination (100 mW cm<sup>-2</sup>). The incident-photon-to-current conversion efficiency (IPCE) measurements were performed without external bias in a two-electrode model under illumination through monochromatic system, composed of a monochromator (Model: 74125, Newport) and light source (Model 73404, Newport). The electrochemical impedance spectra (EIS) were measured using a PGSTAT 302N Autolab Potentiostat/Galvanostat (Metrohm) equipped with a frequency-analyzer module (FRA2) with an excitation signal of 10 mV amplitude.



**Fig. S1** The relationship of concentrated light spot size and generated temperatures.



**Fig. S2** Schematic diagram of fabrication of  $\text{TiO}_2$  NTs.

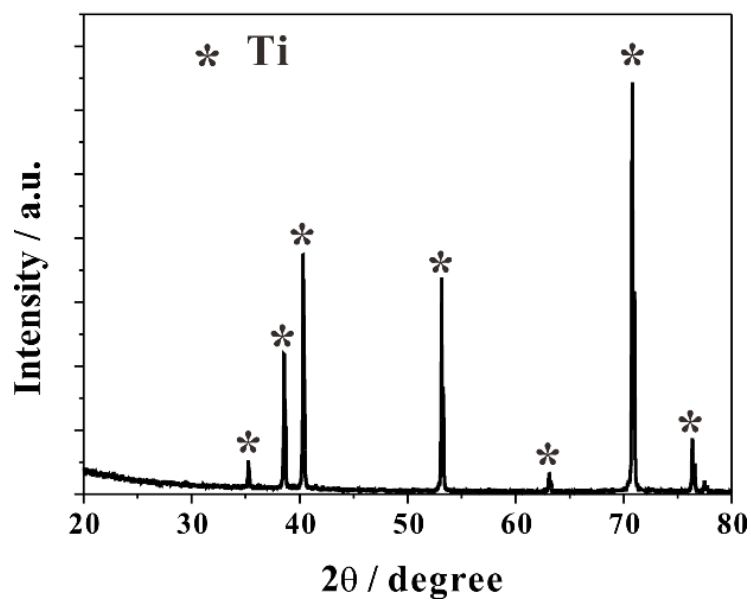


Fig. S3 XRD pattern of as-anodized TiO<sub>2</sub> NTs.

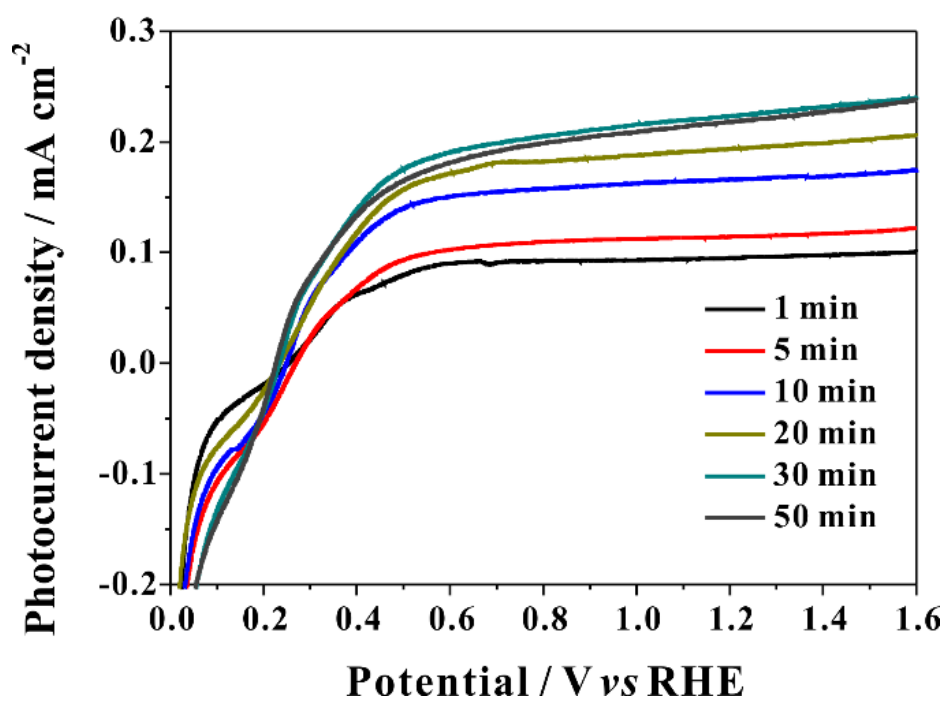
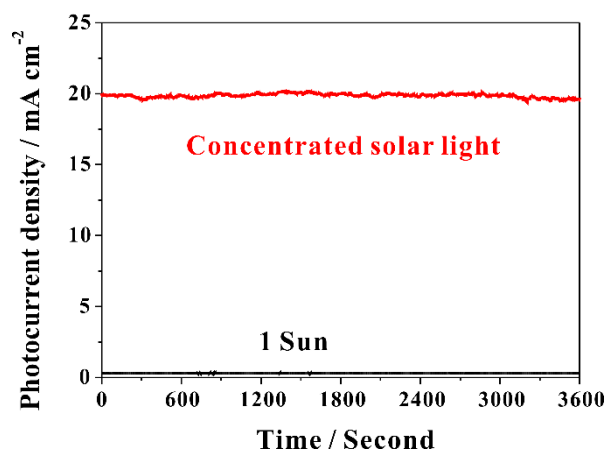
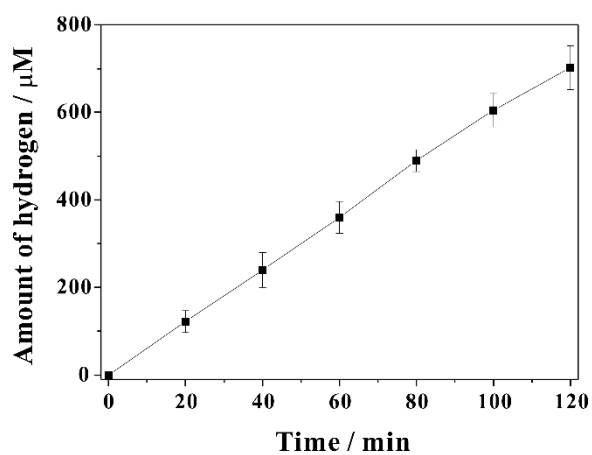


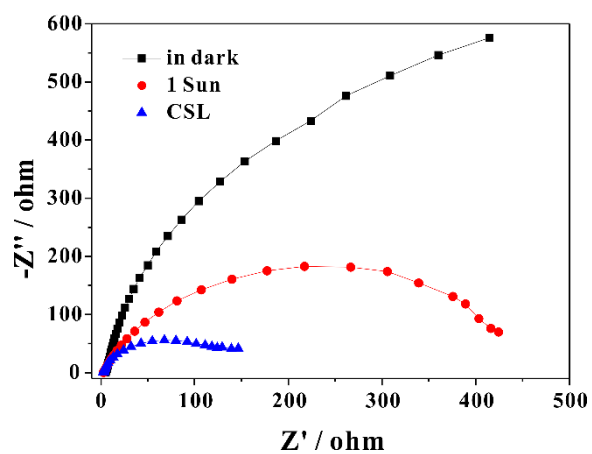
Fig. S4 LSPV of TiO<sub>2</sub> NTs annealed with CSL with different time.



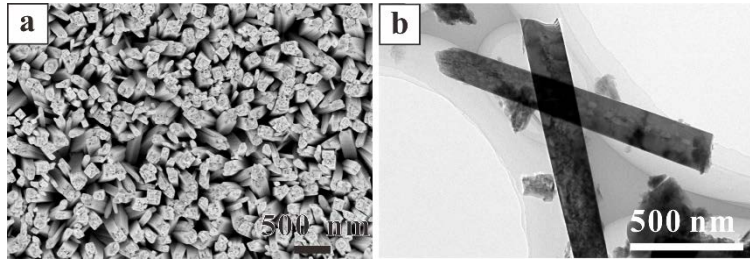
**Fig. S5** Stability measurements of TiO<sub>2</sub> NTs under illumination of 1 Sun and concentrated solar light (CSL).



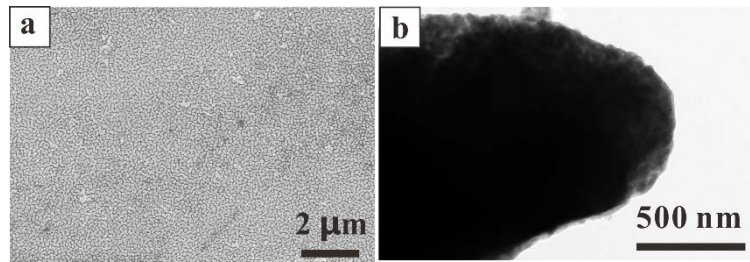
**Fig. 6** Hydrogen generation on TiO<sub>2</sub> NTs under illumination of concentrated solar light.



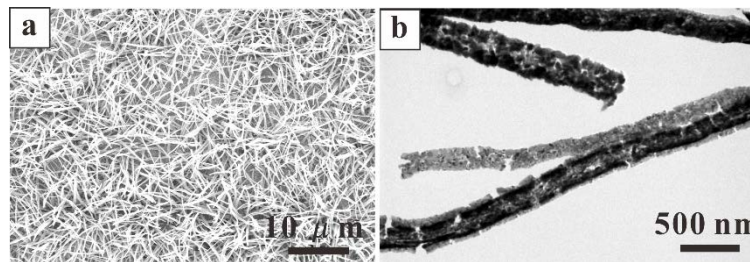
**Fig. 7** Electrochemical impedance spectra of TiO<sub>2</sub> NTs in dark and under illumination of 1 Sun and concentrated solar light (CSL).



**Fig. S8** (a) Top-view SEM image and (b) TEM image of  $\text{TiO}_2$  NWs in large scale.

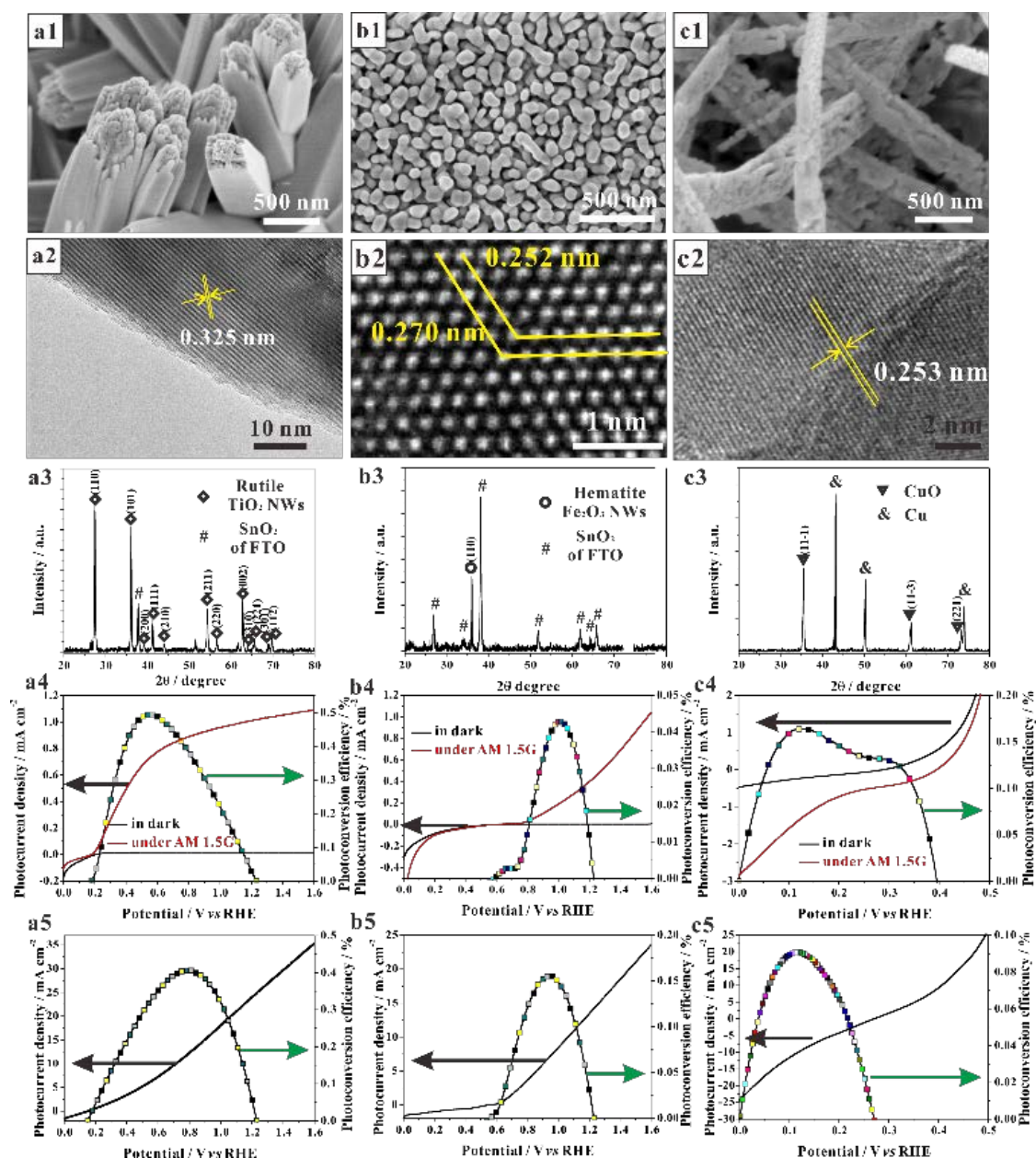


**Fig. S9** (a) Top-view SEM image and (b) TEM image of  $\text{Fe}_2\text{O}_3$  NWs in large scale.

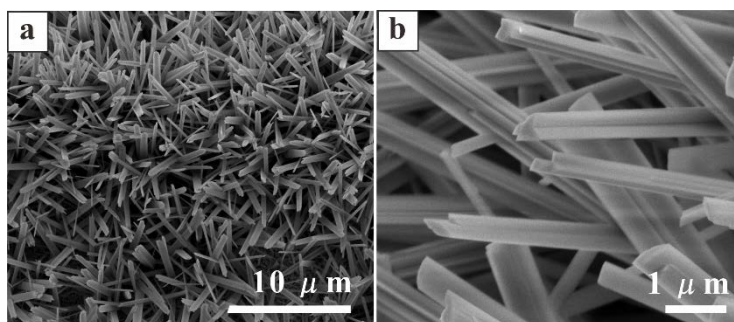


**Fig. S10** (a) Top-view SEM image and (b) TEM image of  $\text{CuO}$  NWs in large scale.





**Fig. S11** (a1) SEM image, (a2) HRTEM image, (a3) XRD pattern, (a4) LSV and photo-conversion efficiency plots on rutile CSL-TiO<sub>2</sub> NWs in dark and under illumination of AM 1.5G, (a5) LSV and photo-conversion efficiency plots of CSL-TiO<sub>2</sub> NWs under illumination of CSL; (b1) SEM image, (b2) HRTEM image, (b3) XRD pattern, (b4) LSV and photo-conversion efficiency plots on hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NWs in dark and under illumination of AM 1.5G, (b5) LSV and photo-conversion efficiency plots of CSL- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> NWs under illumination of CSL; (c1) SEM image, (c2) HRTEM image, (c3) XRD pattern, (c4) LSV and photo-conversion efficiency plots on CSL-CuO NWs in dark and under illumination of AM 1.5G, (c5) LSV and photo-conversion efficiency plots of CSL-CuO NWs under illumination of CSL.



**Fig. S12** Top-view SEM of  $\text{Cu(OH)}_2$  NWs with (a) low and (b) high magnifications.

**Table S1. Summarized PEC data on various CSL-nanomaterials.**

Samples	Under illumination of AM 1.5G		Under illumination of CSL	
	Photocurrent density / $\text{mA cm}^{-2}$	Photo-conversion efficiency / %	Photocurrent density / $\text{mA cm}^{-2}$	Photo-conversion efficiency / %
$\text{TiO}_2$ NTs	0.22	0.13	19.7	0.73
$\text{TiO}_2$ NWs	1.02	0.49	24.9	0.41
$\text{Fe}_2\text{O}_3$ NWs	0.43	0.043	14.2	0.15
$\text{CuO}$ NWs	-2.85	0.16	-24.3	0.091