Supporting Information

Tuning nanosheet Fe_2O_3 photoanode with C_3N_4 and p-type CoO_x decoration for efficient and stable water splitting

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Experimental Section

Fabrication of Fe_2O_3, Fe_2O_3/C_3N_4, and $Fe_2O_3/C_3N_4/CoO_x$ photoanodes: The hematite photoanodes on FTO glass were synthesized by a facile hydrothermal method and microwave-assisted annealing. In a typical process, 40 mL of $FeCl_3 \cdot 6H_2O$ (0.1 M) and Na_2SO_4 (0.05 M) aqueous solution were filled in a Teflon liner with a piece of FTO (3 × 3 cm^2) against the wall, and then the liner was sealed in the stainless autoclave and heated at 80 ˚C for 1.5 h. The naturally cooled yellow FeOOH on FTO was washed with plenty of distilled water and dried at ambient atmosphere. Subsequently, the obtained FeOOH film was cut into several smaller pieces of 2 × 1 cm^2. For the fabrication of Fe_2O_3 photoanode, a hybrid microwave annealing was used with 5.5 g of graphite powder as the susceptor in a Pyrex beaker. The diameter of the beaker is about 3 cm, and the height of graphite powder is about 2 cm in the beaker. The FeOOH film (2 × 1 cm^2) was slightly buried on the flat surface of the graphite and the beaker was heated in a household microwave oven (2.45 GHz and 800 W) for 3 min. The attained Fe_2O_3 film was further cut into pieces in the size of 1 × 0.5 cm^2.

The C_3N_4 semiconductor was synthesized by heating melamine at 550 ˚C for 3 h. Then 0.02 g of the as-synthesized C_3N_4 was put into a metal tungsten boat and set in the vacuum evaporation equipment. Subsequently, a piece of as-synthesized Fe_2O_3 film was set above the metal tungsten boat. When the vacuum degree arrived at about 3×10^{-4} Pa，the C_3N_4 was pre-evaporated at 40 A for 10 min and then at 55 A for 40 min. In order to improve the contact between C_3N_4 and Fe_2O_3, the Fe_2O_3/C_3N_4

composite photoanode was annealed at 350 ˚C for 1 h in the N_2 atmosphere with a ramp rate of 2 ˚C/min.

Finally, 40 mL of $Co(CH_3COO)_2 \cdot 4H_2O$ ethanol solution (1 mmol L^{-1}) was vigorously stirred with 0.4 mL of 25% ammonium hydroxide for 10 min. After that, the solution with the Fe_2O_3/C_3N_4 photoanode was transferred into a Teflon liner. The Teflon liner was sealed and maintained at 120 ˚C for 1 h. When the system was naturally cooled to room temperature, the photoanode was thoroughly washed with distilled water and dried in air.

Characterization: The crystal structure of photoanodes was characterized by XRD using a D8 Advance (Germany) with Cu Kα radiation (λ = 0.15406 nm). The morphology of the samples was characterized by a Zeiss SUPRA-55 scanning electron microscope (SEM). The typical transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were characterized by JEOL 2010 at 300 kV, and the element mapping was characterized under the scanning transmission electron microscopy (STEM) mode. UV-vis diffuse reflectance spectroscopy was recorded with a UV-2450 spectrophotometer. The X-ray photoelectron spectroscopy spectra were recorded by ESCALAB 250Xi equipped with an Al Kα radiation, and all the XPS spectra were adjusted by the graphitic signal to 284.6 eV. The photoluminescence (PL) spectra were measured by a PerkinElmer LS 55 Fluorescence spectrometer.

Photoelectrochemical measurements: The photoelectrochemical measurements were conducted in a CHI604E (Chenhua company, Shanghai) in a three-electrode cell. A

platinum wire and Ag/AgCl (saturated KCl) electrode were employed as the counter electrode and reference electrode, and a hematite photoanode was the working electrode. 1 M sodium hydroxide was used for basic electrolyte (pH = 13.6). The photoanodes were illuminated from the front side using a solar simulator (Perfect Light Corp. Ltd. Beijing) with AM 1.5 G filter and the light power was calibrated to 1 sun (100 mW cm^{-2}). The area of active working photoanode was 0.1 cm^2. The potential can be changed into E_{RHE} according to the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059\,pH + 0.197$$

In this equation, E_{RHE} is the potential *vs.* a reversible hydrogen potential, $E_{Ag/AgCl}$ is the potential *vs.* the Ag/AgCl electrode, and pH is the pH value of the electrolyte.

The photocurrent-potential, electrochemical impedance spectroscopy (EIS), and Mott-Schottky plots (in dark) were measured at the scan rate of 10 mV/s. EIS was conducted by applying an AC voltage amplitude of 10 mV within the frequency range from 100000 to 0.01 Hz with or without light irradiation (100 mW cm^{-2}). For incident photo-to-current conversion efficiency (IPCE) measurements, the cell was irradiated by LED lights (385 nm, 400 nm, 428 nm, 468 nm, 498 nm, 515 nm, and 590 nm), and the values were calculated by the following equation.

$$IPCE = 1240 j_p(\lambda)/\lambda E_\lambda(\lambda)$$

In which $j_p(\lambda)$ is the measured photocurrent density (mA cm^{-2}), and $E_\lambda(\lambda)$ is the power density of the incident light (mW cm^{-2}) for each wavelength, λ (nm).

Results

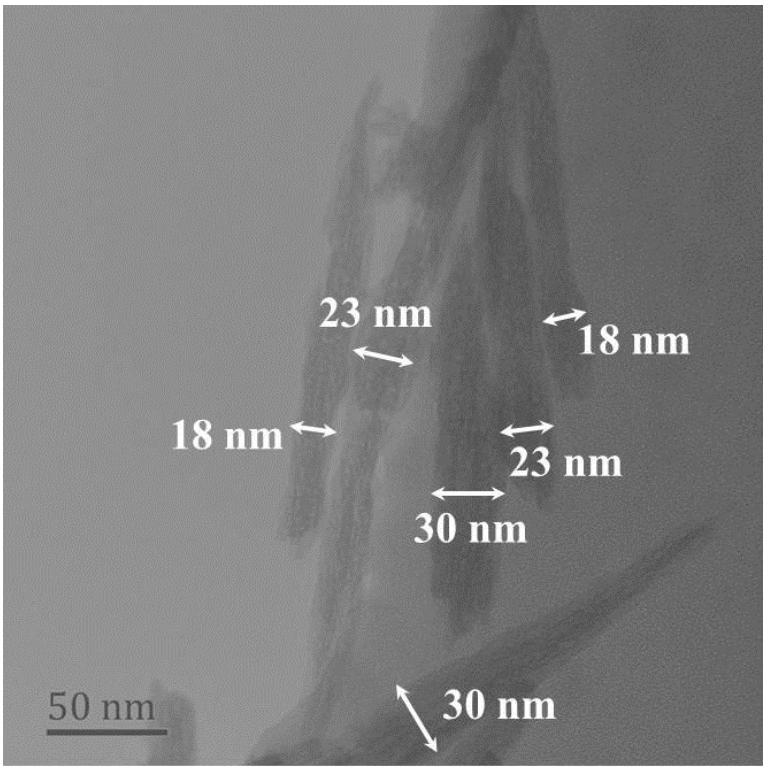

Fig. S1 Typical TEM image of the as-synthesized FeOOH on a FTO substrate.

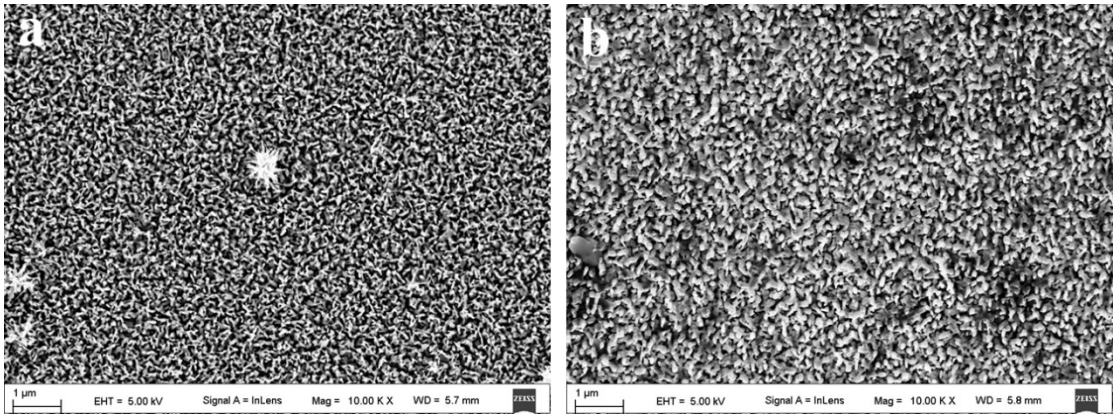

Fig. S2 SEM images of Fe_2O_3 and Fe_2O_3/C_3N_4.

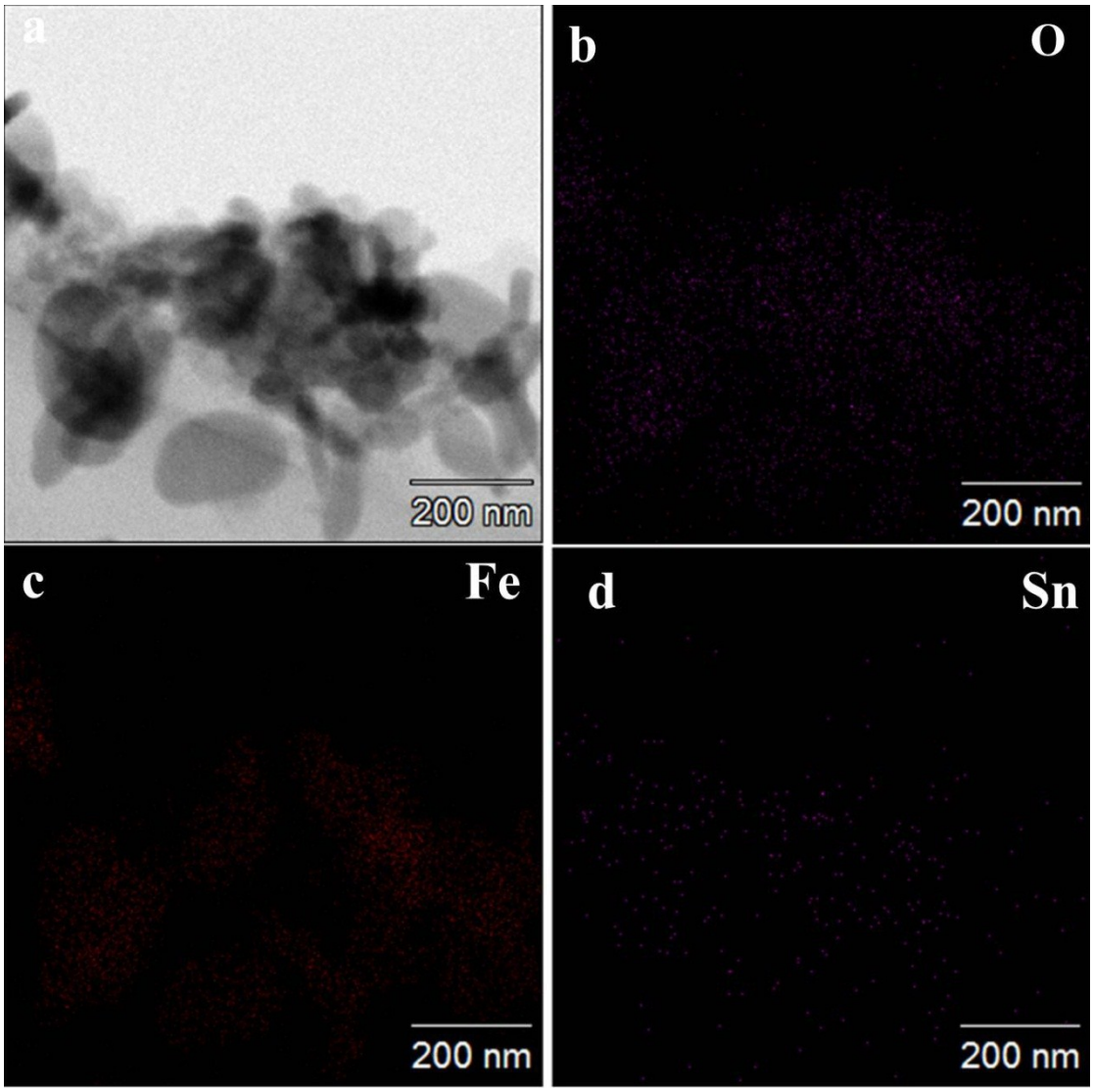

Fig. S3 a) the scanning transmission electron microscopy (STEM) image, and b) O, c) Fe, and Sn elements mapping.

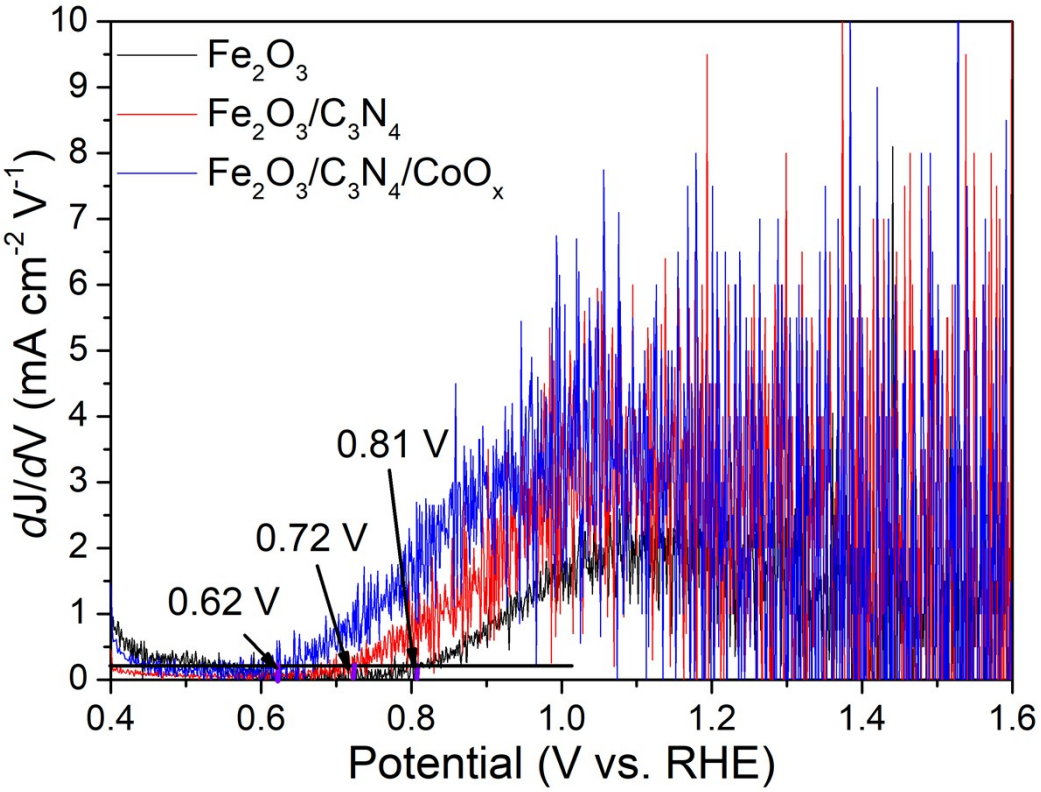

Fig. S4 First-order derivative curves of the photocurrent densities as a function of the voltage (d*J*/d*V* curves) for Fe_2O_3, Fe_2O_3/C_3N_4, and $Fe_2O_3/C_3N_4/CoO_x$.

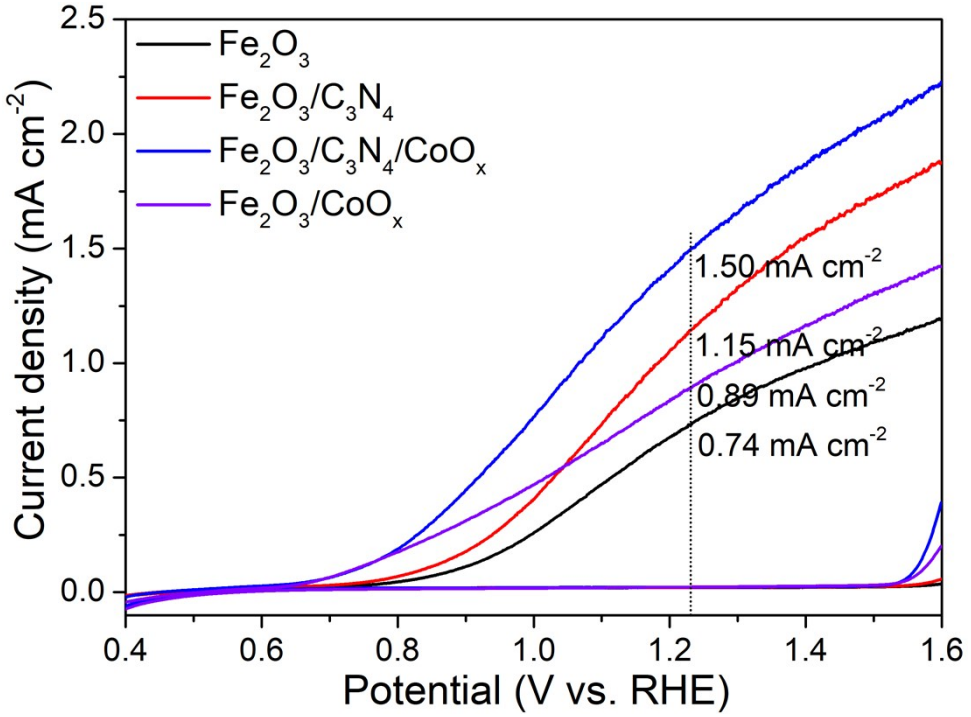

Fig. S5 Linear sweep voltammograms of Fe_2O_3, Fe_2O_3/C_3N_4, $Fe_2O_3/C_3N_4/CoO_x$, and Fe_2O_3/CoO_x. Electrolyte: 1 M of NaOH (pH = 13.6), Light source: AM 1.5 G (100 mW cm^{-2}), Scan rate: 10 mV s^{-1}.

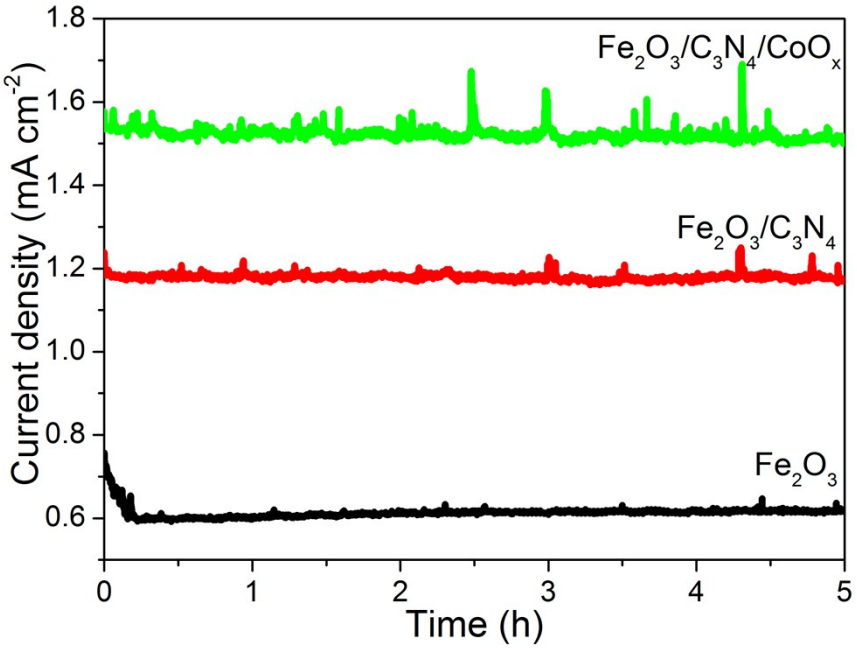

Fig. S6 Photoelectrochemical stability of Fe_2O_3, Fe_2O_3/C_3N_4, and $Fe_2O_3/C_3N_4/CoO_x$ photoanodes at 1.23 V_{RHE}. Electrolyte: 1 M of NaOH (pH = 13.6), Light source: AM 1.5 G (100 mW cm^{-2}).

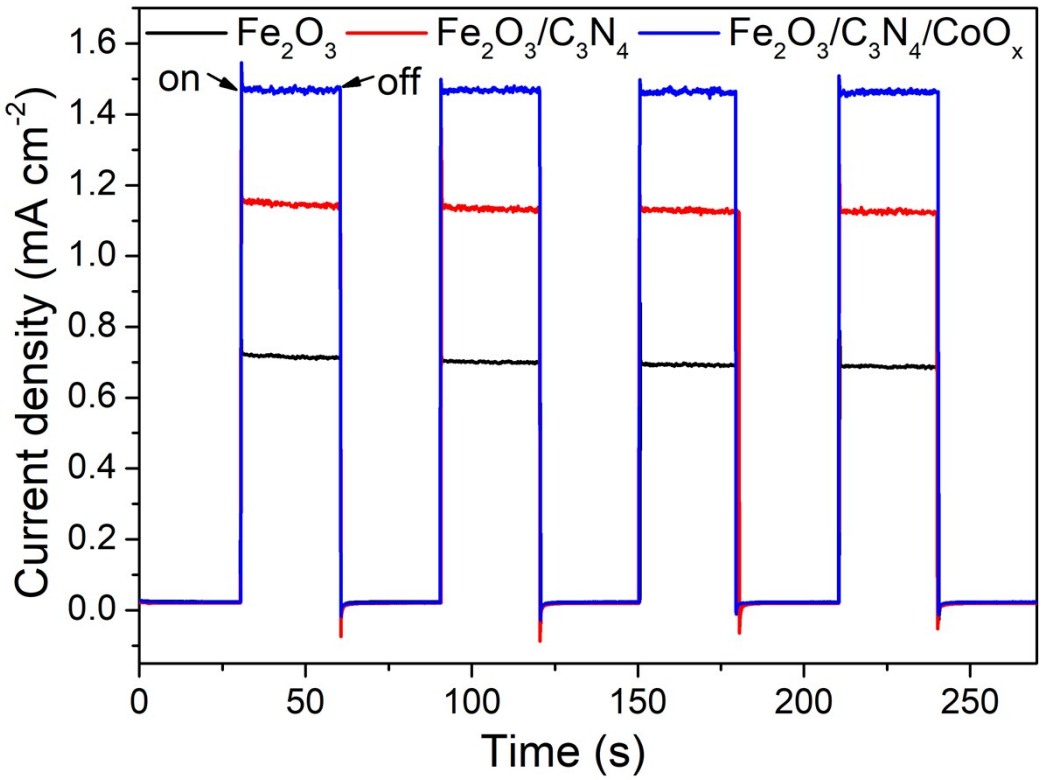

Fig. S7 Photocurrent density-potential curves as a function of time of Fe_2O_3, Fe_2O_3/C_3N_4, and $Fe_2O_3/C_3N_4/CoO_x$ photoanodes at 1.23 V_{RHE} under chopped illumination. Electrolyte: 1 M of NaOH (pH = 13.6), Light source: AM 1.5 G (100 mW cm^{-2}).

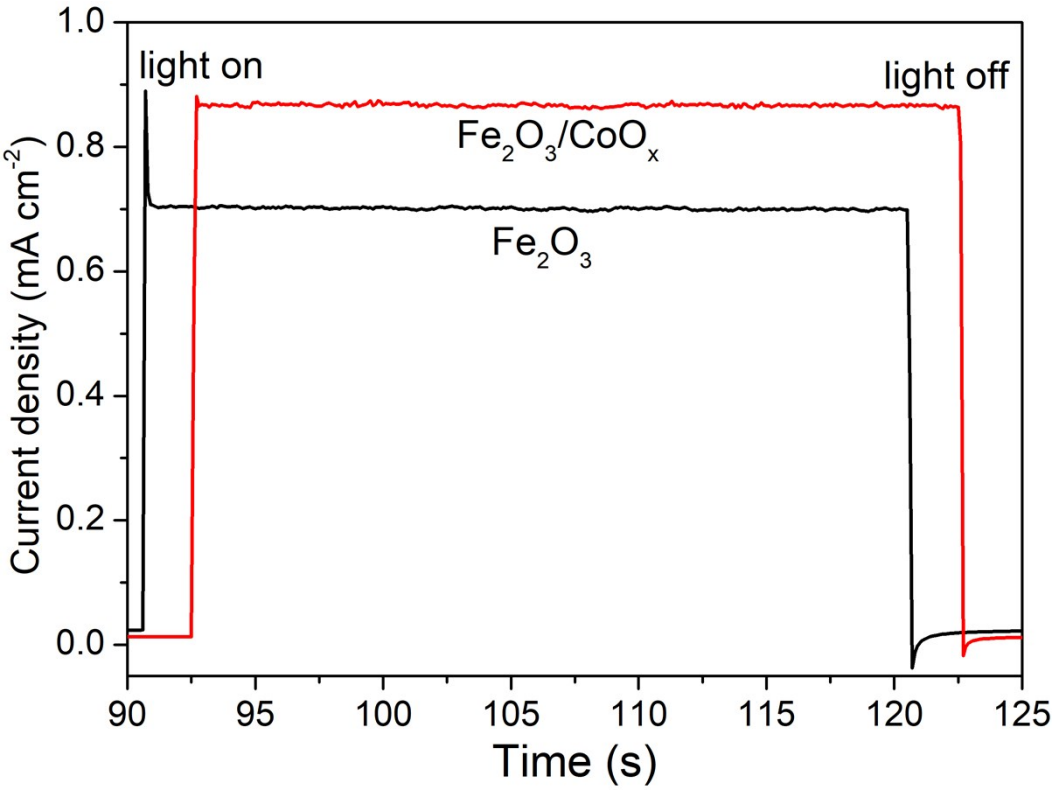

Fig. S8 Photocurrent density-potential curves as a function of time of Fe_2O_3 and Fe_2O_3/CoO_x photoanodes at 1.23 V_{RHE} under chopped illumination. Electrolyte: 1 M of NaOH (pH = 13.6), Light source: AM 1.5 G (100 mW cm^{-2}), Scan rate: 10 mV/s.

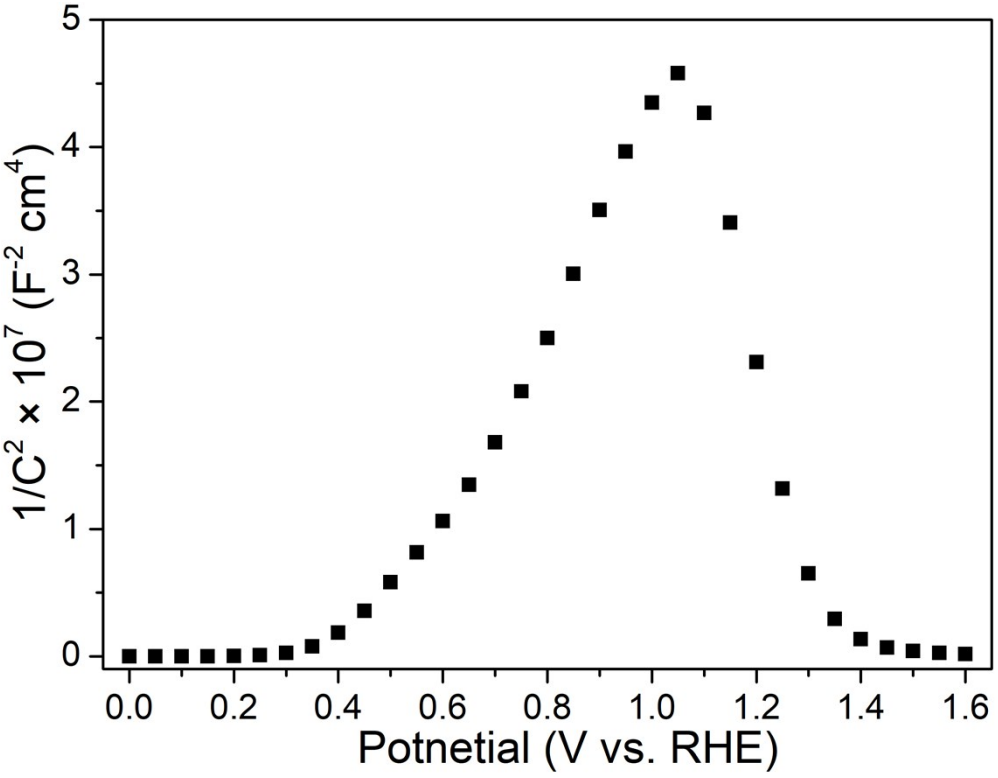

Fig. S9 Mott-Schottky plots of Fe_2O_3/CoO_x photoanode. Frequency: 1 kHz; Electrolyte: 1 M of NaOH.

Table S1. The photocurrent density of Fe_2O_3, Fe_2O_3/C_3N_4, and $Fe_2O_3/C_3N_4/CoO_x$ at different wavelength of LED light.

Wavelength (nm)	Power density ($mW\ cm^{-2}$)	Photocurrent density ($mA\ cm^{-2}$)		
		Fe_2O_3	Fe_2O_3/C_3N_4	$Fe_2O_3/C_3N_4/CoO_x$
385	28	2.39	4.4	7.10
400	1.4	0.10	0.17	0.28
428	4.3	0.26	0.42	0.66
468	6	0.21	0.36	0.54
498	5	0.11	0.20	0.30
515	3.5	0.06	0.10	0.19
590	15.3	0.06	0.07	0.15