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Supporting Information

Highly Efficient Photoelectrochemical H_2O_2 Production Reaction with Co_3O_4 as Co-catalysts

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Experimental section

Synthesis of TiO_2 NRs. Synthesis of TiO_2 on FTO using a facile hydrothermal method has been described previously. Briefly, 20 mL of deionized water and 20 mL of concentrated hydrochloric acid (36.5-38.0 wt%) were mixed and stirred for 5 min, then 0.65 mL of titanium butoxide was added dropwise to the mixed solution. After stirring for another 5 min, 3.35 mL of a NaCl aqueous solution (5 M) was added to the solution and then the mixture was stirred for another 5 min. The solution was averagely transferred to two Teflon-lined stainless steel autoclaves (50 mL), where a FTO substrate ($5 * 1$ cm^2) was placed at an angle against the wall of the Teflon-lined with the conducting side facing down. The hydrothermal synthesis was conducted at 150 °C for 10 h, followed by flowing water cooling to room temperature. Afterwards, the FTO substrate was taken out, rinsed with deionized water and dried in ambient air. Finally, the TiO_2 NRs were annealed in air at 500 °C for 2 h.

Synthesis of Co_3O_4 nanopsrticles. The Co_3O_4 nanoparticles were synthesized by a facile hydrothermal method. In a typical procedure, 0.4 mL ammonium solution ($NH_3{\bullet}H_2O$, 25 wt%) was added into 25 mL 1 mM cobalt acetate aqueous solution, followed by stirring for 15 min. Then, the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave. The hydrothermal synthesis was conducted at 150 °C for 1h. After the stainless autoclave was cooled to room temperature by flowing water, the obtained products were centrifuged, washed with deionized water and ethanol for three times, respectively. Lastly, the obtained samples were dried in 80 °C for several hours in a drying oven.

Synthesis of Co_3O_4/TiO_2 NRs. The drop-casting technique was used to synthesize the Co_3O_4/TiO_2 composites. Firstly, 4 mg of Co_3O_4 nanoparticles were dispersed in 100 mL absolute ethanol and sonicated for 30 min to form “Co solution”. The “Co solution” was then drop-casted onto the TiO_2 electrodes. The drop-casted area was controlled to be 1 cm^2 and the mass of Co_3O_4 was adjusted by the drop volume of “Co solution”. The composites were annealed at 500 °C for 2 h. Before applying the “Co solution”, the mass of TiO_2 film in 1 cm^2 was determined to be 0.42 ± 0.03 mg by comparing the mass of FTO substrates and TiO_2 electrodes using 10 samples prepared in the same conditions. The Co_3O_4 concentration of “Co solution” was known. Therefore, the loading weight of Co_3O_4 could be accurate controlled by adjusting the drop volume of “Co solution”. In order to investigate the effects of Co_3O_4 loading on the PEC tests, the Co_3O_4/TiO_2 composites with various Co_3O_4 loading weight (0.12, 0.25, 0.5, 2, 3.75, and 7.5 wt%) were prepared.

Synthesis of Co_3O_4/WO_3 nanoflakes. WO_3 nanoflakes were synthesized by a modified hydrothermal method. Briefly, a seed solution prepared by dissolving 1.25 g of H_2WO_4 and 0.5 g of poly(vinyl alcohol) (PVA) into 17 mL of H_2O_2 (30 wt%) was spin-coated onto fluorine-doped tin oxide substrates at 1000 rpm, followed by annealing at 500 °C in air for 2 h. Another H_2WO_4 solution was prepared by adding 1.25 g of H_2WO_4 and 17 mL of H_2O_2 (30 wt%) into 25 mL of H_2O and stirred at 95 °C to dissolve. This H_2WO_4 solution was then diluted to 0.05 M for the hydrothermal process. In order to prepared the hydrothermal precursor solution, 3 mL of H_2WO_4 (0.05 M), 0.02 g of oxalic acid, 0.02 g of urea, 12.5 mL of acetonitrile, and 0.5 mL of HCl (6 M) were added into a 50 mL breaker and stirred to clear. An FTO substrate precoated with WO_3 seed was placed into a 50 mL Teflon-lined stainless steel autoclave filled with the as-prepared precursor solution, which was then kept at 180 °C for 2 h. Finally, the obtained sample was annealed at 500 °C in air for 2 h. The Co_3O_4/WO_3 composites are synthesized by the same method of Co_3O_4/TiO_2. The loading weight of Co_3O_4 on WO_3 nanoflakes is about 0.25 wt%.

Physical Characterization. X-ray diffraction patterns were recorded with a Bruker D8 Focus operating at 40 kV and 40 mA equipped with a nickel-filtered Cu Kα radiation ($\lambda = 1.54056$ Å) and operating in a 2θ range of 20 – 70 ° at a scan rate of 8 per minute. The morphologies were characterized by field emission scanning electron microscope (FESEM, S-4800). Elemental analysis was carried out by energy dispersive spectroscopy (EDS) at 15 kV. TEM was performed on a JEOL JEM 2100F electron microscope operating at 200 kV. UV–visible reflectance spectra and transmittance spectra of Bi-based electrode were obtained on a SHIMADZU UV-2550 spectrophotometer.

Photoelectrochemical Measurements. PEC measurements were performed in 0.5 M $KHCO_3$ (pH 7.6) using a standard quartz 3-electrode cell with Pt foil as the counter electrode, Ag/AgCl as the reference electrode and the Co_3O_4/TiO_2 or Co_3O_4/WO_3 phototelectrodes as the working electrode. In our lab, the Ag/AgCl electrode must be covered with black insulated rubber tape in order to avoid the Ag/AgCl electrode being irradiated by the strong light. In order to simulate sunlight, a 300 W xenon lamp (PE300BUV, CERMAX) equipped with an AM 1.5G filter was used as the light source, and the power intensity of the light was calibrated to 100 mW cm^{-2}. An electrochemical workstation (IVIUM CompactStat.e20250) was used to measure the current-voltage (I-V) characteristic of the electrode, with a scan rate of 50 mV s^{-1}.

Detection of the amount of hydrogen peroxide evolution. To quantitatively determine the amount of H_2O_2 produced from the oxidation of water, a three-electrode system was employed. An aqueous 0.5 M $KHCO_3$ (pH 7.6) was used as the electrolyte solution. The sample was irradiated under AM 1.5G illumination (100 mW cm^{-2}). After 3 h reaction at 1.23 V *vs.* RHE, the 5 mL electrolyte was added into 5 mL solution containing 10^{-3} M $FeSO_4$ and 1 M HCl and this solution was stirred for 10 min. We can quantify the amount of H_2O_2 by detecting Fe^{3+} which is oxidized from Fe^{2+} by H_2O_2 (eq S1).

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + H_2O \qquad \text{(S1)}$$

The characteristic peaks of Fe^{2+} and Fe^{3+} are located on 250 nm and 290 nm in UV-visible diffusive reflectance spectra. According to the absorbance of Fe^{3+}, the concentration of Fe^{2+} can be calculated.

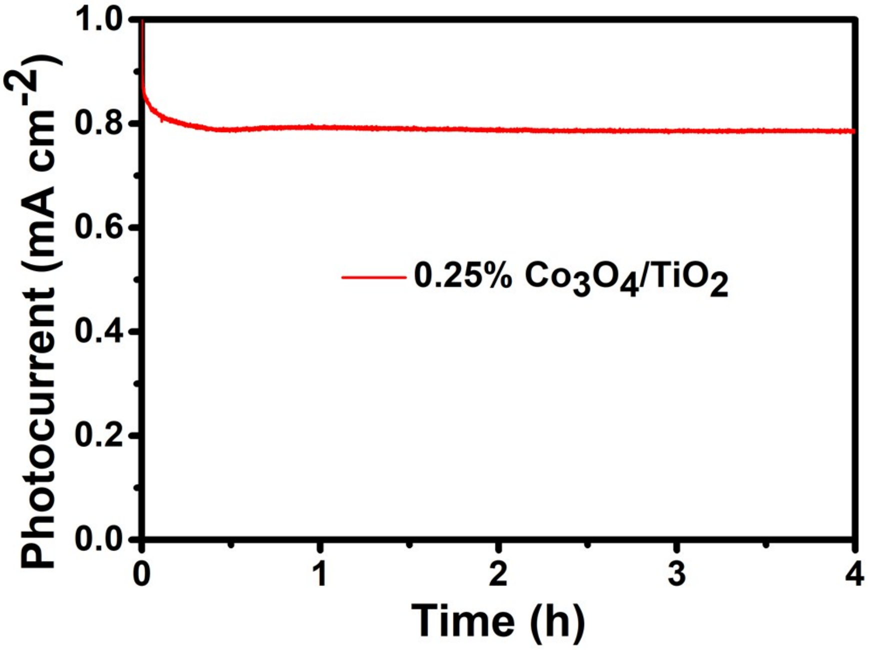

Fig. S1. Photocurrent-time (J-t) curves of the 0.25% Co_3O_4/TiO_2 sample in a 0.5 M $KHCO_3$ aqueous electrolyte (pH 7.6) under AM 1.5G at a constant applied bias of 1.23 V *vs.* RHE.

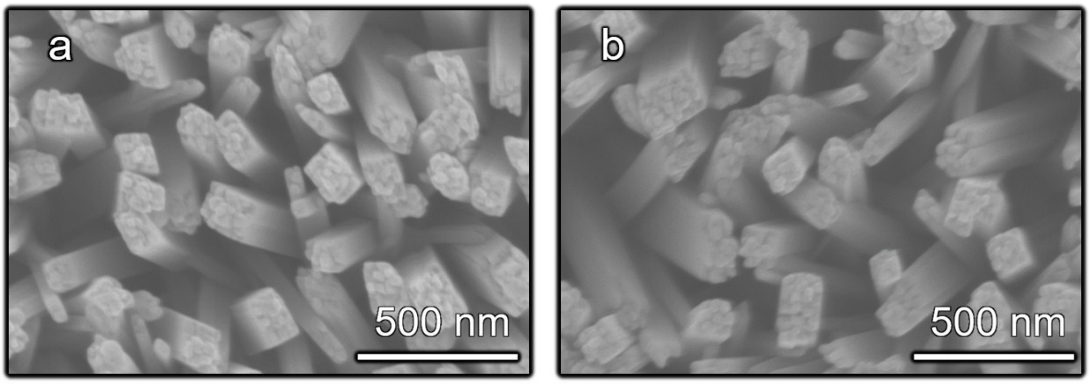

Fig. S2. SEM images of the 0.25% Co_3O_4/TiO_2 sample (a) before and (b) after photocurrent-time test.

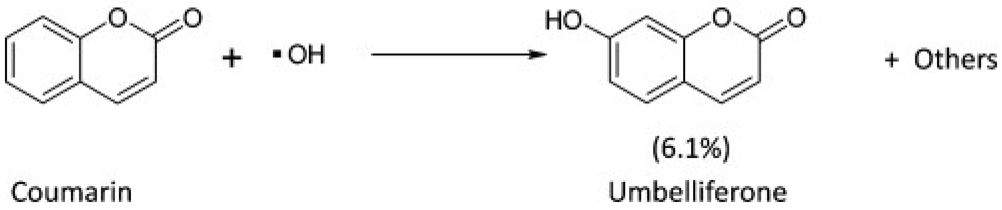

Fig. S3. Reaction for detecting OH radicals in solution with coumarin.

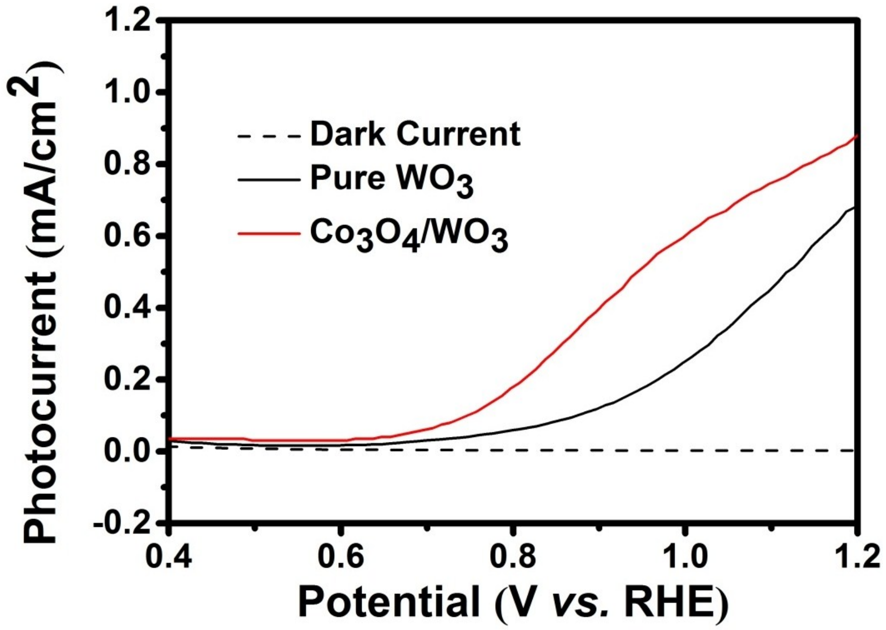

Fig. S4. J-V curves of WO_3 nanoflake and Co_3O_4/WO_3 samples under AM 1.5G irradiation in a 0.5 M $KHCO_3$ aqueous electrolyte (pH 7.6).

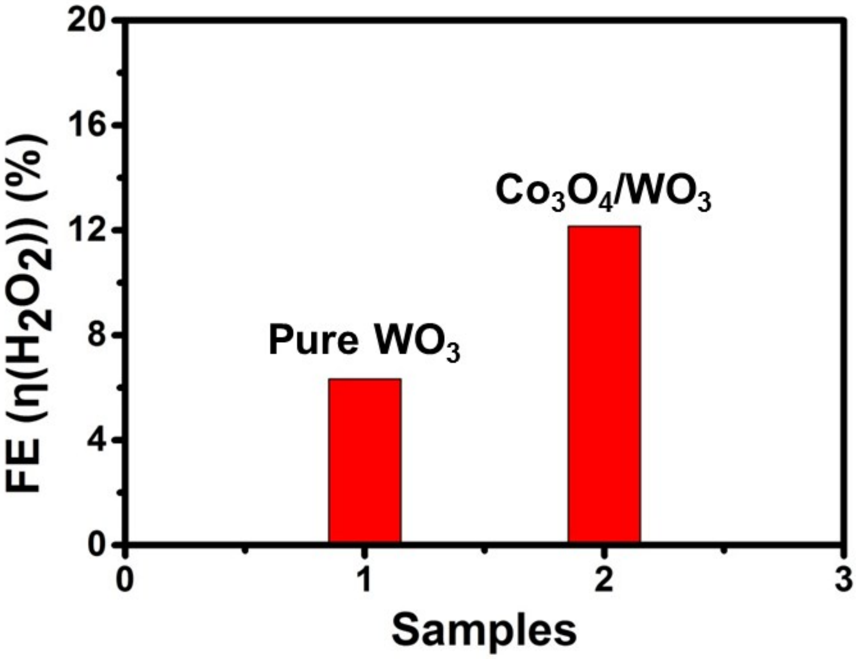

Fig. S5. The calculated η(H_2O_2) of WO_3 nanoflake and Co_3O_4/WO_3 samples under AM 1.5G irradiation in a 0.5 M $KHCO_3$ aqueous electrolyte (pH 7.6).

Table S1. Average atomic ratios (metal basis) in the 0.25% Co_3O_4/TiO_2 electrode before and after photocurrent-time test obtained by EDS analysis.

	Before Test	After Test
Average ratio	Co:Ti=401.33:1	Co:Ti=400.79:1