Highly Efficient Photoelectrochemical H₂O₂ Production Reaction with Co₃O₄ 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$_3$O$_4$ nanoparticles. The Co$_3$O$_4$ nanoparticles were synthesized by a facile hydrothermal method. In a typical procedure, 0.4 mL ammonium solution (NH$_3$•H$_2$O, 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 1 h. 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$_3$O$_4$/TiO$_2$ NRs. The drop-casting technique was used to synthesize the Co$_3$O$_4$/TiO$_2$ composites. Firstly, 4 mg of Co$_3$O$_4$ 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$_3$O$_4$ 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$_3$O$_4$ concentration of “Co solution” was known. Therefore, the loading weight of Co$_3$O$_4$ could be accurate controlled by adjusting the drop volume of “Co solution”. In order to investigate the effects of Co$_3$O$_4$ loading on the PEC tests, the Co$_3$O$_4$/TiO$_2$ composites with various Co$_3$O$_4$ loading weight (0.12, 0.25, 0.5, 2, 3.75, and 7.5 wt%) were prepared.

Synthesis of Co$_3$O$_4$/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$_2$WO$_4$ and 0.5 g of poly(vinyl alcohol) (PVA) into 17 mL of H$_2$O$_2$ (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$_2$WO$_4$ solution was prepared by adding 1.25 g of H$_2$WO$_4$ and 17 mL of H$_2$O$_2$ (30 wt%) into 25 mL of H$_2$O and stirred at 95 °C to dissolve. This H$_2$WO$_4$ solution was then diluted to 0.05 M for the hydrothermal process. In order to prepared the hydrothermal precursor solution, 3 mL of H$_2$WO$_4$ (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\(_3\)O\(_4\)/WO\(_3\) composites are synthesized by the same method of Co\(_3\)O\(_4\)/TiO\(_2\). The loading weight of Co\(_3\)O\(_4\) 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 Ka radiation (\(\lambda = 1.54056 \text{ Å}\)) and operating in a 20 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\(_3\)O\(_4\)/TiO\(_2\) or Co\(_3\)O\(_4\)/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\(_2\)O\(_2\) 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\(_2\)O\(_2\) by detecting Fe\(^{3+}\) which is oxidized from Fe\(^{2+}\) by H\(_2\)O\(_2\) (eq S1).

\[
2\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O}
\]  
(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$_3$O$_4$/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$_3$O$_4$/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$_3$O$_4$/WO$_3$ samples under AM 1.5G irradiation in a 0.5 M KHCO$_3$ aqueous electrolyte (pH 7.6).
Fig. S5. The calculated $\eta(H_2O_2)$ of WO$_3$ nanoflake and Co$_3$O$_4$/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$_3$O$_4$/TiO$_2$ electrode before and after photocurrent-time test obtained by EDS analysis.

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<thead>
<tr>
<th>Average ratio</th>
<th>Before Test</th>
<th>After Test</th>
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<tbody>
<tr>
<td>Co:Ti=401.33:1</td>
<td>Co:Ti=400.79:1</td>
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