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Development of an alkaline Electro-Fenton process based on the synthesis of H_2O_2 in bicarbonate electrolyte

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Material preparation. The In_2O_3 films were prepared on fluorine-doped tin oxide (FTO) glass substrate (1 cm×2 cm, sheet resistance < 15 Ω) by a drop-casting method that similar to a previous report.[1] Specifically, $In(NO_3)_3 \cdot xH_2O$ (Aladdin, 99.9%) was firstly dissolved in ethanol to form 0.1 M In^{3+} precursor solution. Then, 80 μL of In^{3+} precursor solution was dropped on the conductive surface of FTO glass, and successively heated in air at 150 °C for 60 min and 300 °C for 60 min to form In_2O_3 film.

The MnO_2 powders were prepared by a hydrothermal method as reported in our previous work.[2] Firstly, 0.845 g $MnSO_4 \cdot H_2O$ (Aladdin, 99%) and 1.14 g $(NH_4)_2S_2O_8$ (Aladdin, >98%) were dissolved in 80 mL of deionized water. Then, this precursor solution was transferred into a Teflon-lined autoclave (150 mL) for hydrothermal reaction at 140 °C. After 12 h of reaction, the products were collected through centrifugation and washed with deionized water. Finally, the resultant products were dried at 80 °C for 5 h, and further annealed in air at 300 °C for 3 h.

Material characterizations. The morphology of In_2O_3 films and MnO_2 powders was observed by scanning electron microscope (SEM, Carl Zeiss GeminiSEM 300). The diffraction (XRD) patterns of samples were recorded on an X-ray diffractometer (XRD-6000, Shimadzu). In addition, the chemical state of the In_2O_3 films and MnO_2 powders were examined with X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific). The content of dissolved In and Mn after reaction in electrolyte was analyzed by inductively coupled plasma spectrometer (ICP, Thermo ICAP6300 Duo).

The electrochemical production of H_2O_2 and related detection. The electrochemical production of H_2O_2 was performed on a CHI 760E workstation with a standard three-electrode cell. The resultant In_2O_3 film with an geometric area of 1.0 cm×1.0 cm was used as the working electrode, a graphite rod (ϕ =5 mm) was acted as the counter electrode, and the reference electrode was a saturated calomel electrode (SCE, Shanghai INESA Scientific Instrument). 2.0 M $KHCO_3$ aqueous solution was used as the electrolyte. For all electrochemical testing, the electrolyte volume was fixed at 25 mL. The concentration of electrochemically produced H_2O_2 was doubly detected by a $TiOSO_4$ UV-vis spectrometer method and commercial H_2O_2 strips testing. Firstly, 0.5 mL of electrolyte was collected from cell, and then 1.0 mL of 3.0 M H_2SO_4 was added into the electrolyte to adjust its pH to acidity. After that, 1.0 mL of 0.1 M $TiOSO_4$ was added and reacted with the collected electrolyte for 10 min. Finally, the concentration of H_2O_2 was determined by UV-vis spectrometer (Beijing Persee TU-1901, China) at a wavelength of 402 nm. The commercial H_2O_2 strips were purchased from HangZhou Lohand Biological *Co.*, LTD.

The Faraday efficiency (FE) of H_2O_2 production by the In_2O_3 film anode at different potentials was calculated on the basis of the actual production of H_2O_2 and theoretical production of H_2O_2. The theoretical production of H_2O_2 was calculated using the recorded charge assuming it all originate from the 2-electrons oxidation of water into H_2O_2. The actual production of H_2O_2 was determined by $TiOSO_4$ UV-vis spectrometer method. The equation is as follows.

$$FE = \frac{amount\ of\ generated\ H_2O_2}{theoretical\ amount\ of\ H_2O_2} \times 100\% \qquad (1)$$

The measured potentials (E_{SCE}) *vs.* SCE reference electrode were calibrated into the potentials *vs.* reversible hydrogen electrode (E_{RHE}) using Nernst equation as follow.

$$E_{\mathrm{RHE}} = E^{\theta}_{\mathrm{SCE}} + E_{\mathrm{SCE}} + 0.0592\, pH \qquad (2)$$

Where $E^{\theta}_{\mathrm{SCE}} = 0.241$ V *vs.* RHE, at 298 K, and *pH* is the pH value of electrolyte.

The electrochemically active surface area (ECSA) of the In_2O_3 film in 1.0 M $KHCO_3$, Na_2HPO_4 and Na_2SO_4 electrolyte was determined based on its double capacitance (C_{dl}). in a non-Faradaic potential range of 0.65 to 0.75 V *vs.* RHE, C_{dl} was determined from the cyclic voltammograms (CV) at a series of scan rates of 20, 40, 60, 80, 100 mV/s (**Fig. S3a, S3b** and **S3c**). The anodic-cathodic current density (ΔI) at 0.7 V *vs.* RHE and the scan rate extracted from the CV curves were fitted into a linear relationship (**Fig. S3h**), and the value of C_{dl} was half of the slope of ΔI *vs* scan rate curve. The ECSA of the In_2O_3 film was calculated using the following equation:

$$\mathrm{ECSA} = C_{dl}/C_s \qquad (3)$$

where C_s represents the specific capacitance of In_2O_3 film electrode in theory. Because the surface of In_2O_3 film electrode is not as smooth as expected, the C_s value of In_2O_3 electrodes was replaced by the C_s value of FTO substrate in 1.0 M $KHCO_3$, Na_2HPO_4 and Na_2SO_4 electrolyte (**Fig. S3g**) to calculate the ECSA.

The degradation of organics. P-nitrophenol (PNP), Bisphenol A (BPA) and Rhodamine B (RhB) were selected as model organic pollutants to demonstrate the effectiveness of the as-proposed alkaline Electro-Fenton process, because PNP, BPA and RhB can exist in the HCO_3^--containing aqueous solution stably. The degradation of PNP, BPA and RhB was conducted at constant potential model in a standard three-electrode cell, respectively. The exposed geometric area of In_2O_3 film working electrode was 1.0 cm^2 (1.0 cm×1.0 cm), the counter and reference electrode were graphite rod and SCE electrode, respectively. For all of degradation reactions, the electrolyte volume was fixed at 25 mL, the rotated speed was 200 rpm and the MnO_2 content was 0.6 g/L.

The scale-up degradation experiment was performed in a two-electrodes cell linked with a DC power. An In_2O_3 film with an area of 4.0 × 5.0 cm^2 was used as the anode, a graphite rod (5 mm diameter× 80 mm length) was acted as the cathode. The electrolyte was 150 mL of 2.0 M $KHCO_3$/10 ppm RhB with 0.6 g/L MnO_2 powders, and the DC voltage was fixed at 5.0 V.

The concentration changes of PNP and RhB were detected by UV-vis spectrometer method at a wavelength of 401 nm and 554 nm, respectively. The concentration change of BPA was detected by high-performance liquid chromatography (HPLC, Shimadzu, LC-16). The mobile phase was methanol and water (70:30 v/v), and the flow rate was 1 mL/min, and the detection wavelength was 230 nm. The TOC removal of electrolyte was checked by TOC analyzer (Shimadzu, TOC-L CPH). In addition, the active radicals in $KHCO_3/H_2O_2$ and $KHCO_3/H_2O_2/MnO_2$ solution were detected by a Bruker EMX Plus-10/12 EPR spectrometer, respectively. The ^{13}C NMR signals of HCO_3^- and HCO_4^- in $KHCO_3$ electrolyte were detected by NMR instrument (Bruker BioSpin, 600M HZ) at room temperature.

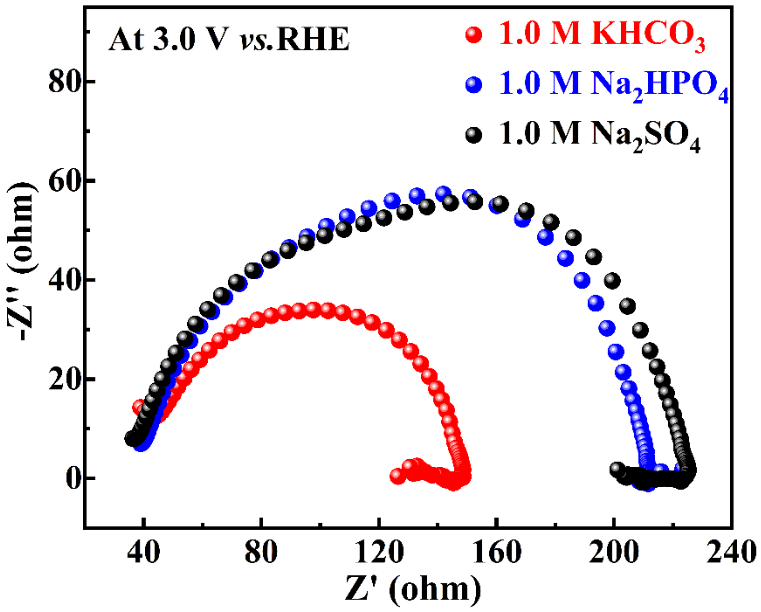

Fig. S1 The Nyquist plots of the In_2O_3 film electrode in 1.0 M $KHCO_3$, Na_2HPO_4 or Na_2SO_4 electrolyte at 3.0 V *vs.* RHE.

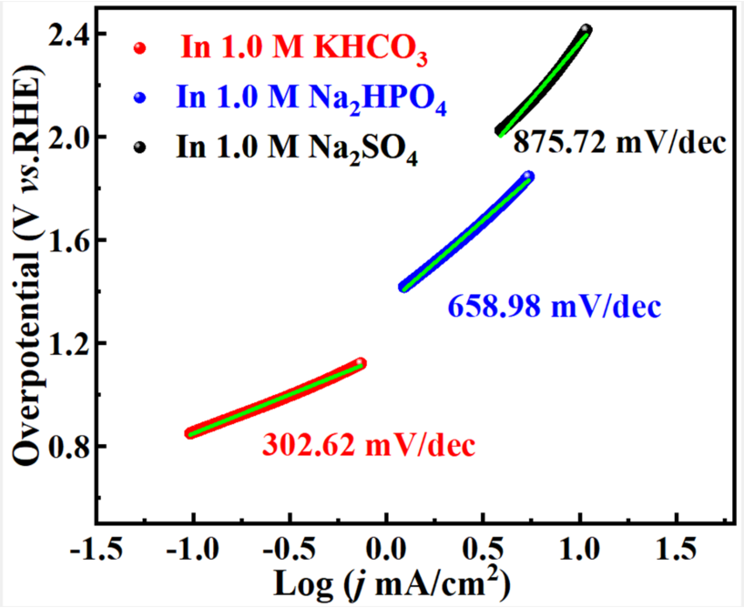

Fig. S2 The Tafel curves of the In_2O_3 film electrode in 1.0 M $KHCO_3$, Na_2HPO_4 or Na_2SO_4 electrolyte, taking the oxidation of water into oxygen (1.23 V *vs.* RHE) as the reference.

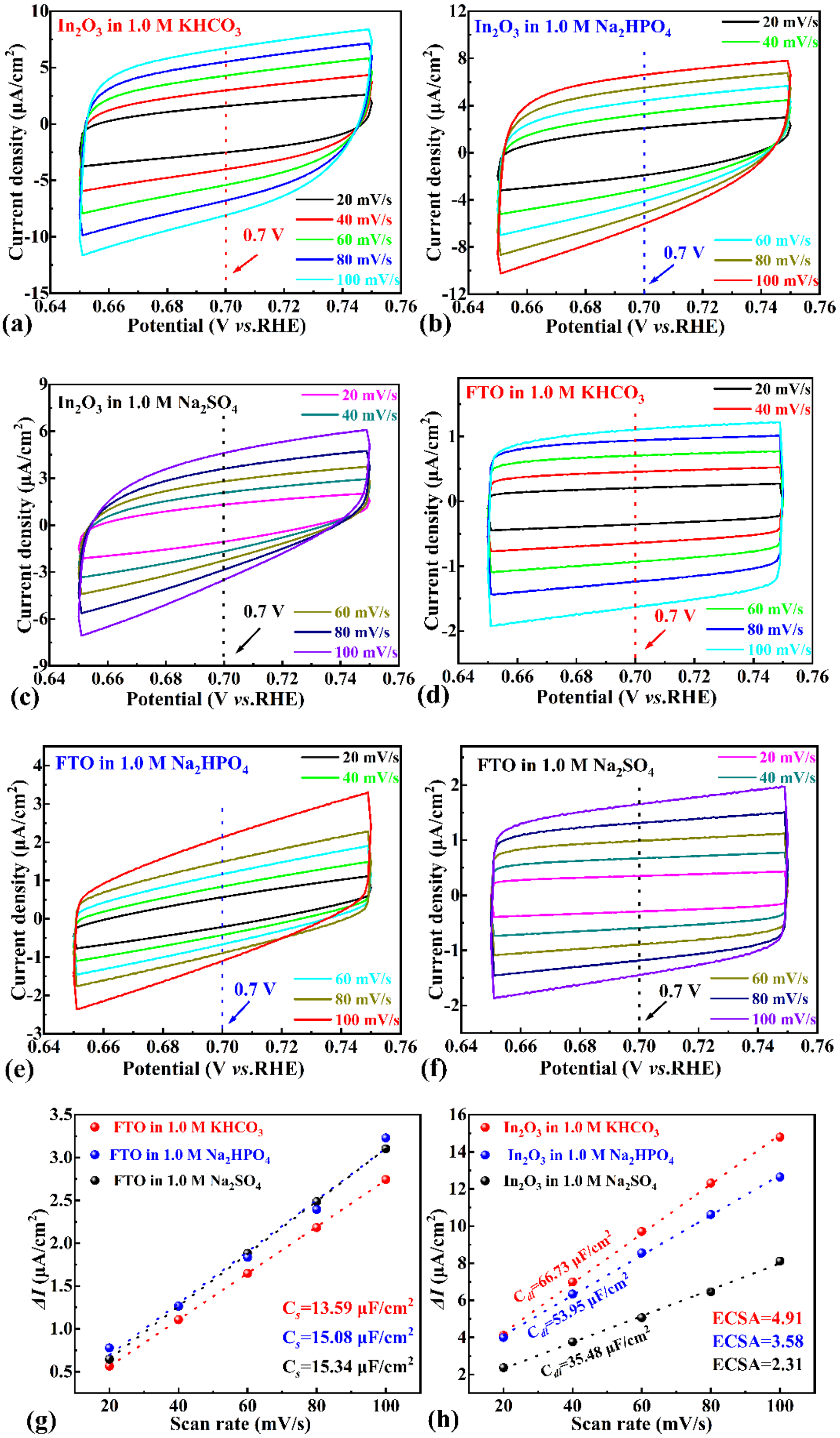

Fig. S3 CV curves of In_2O_3 (a-c) and FTO (d-f) in 1.0 M $KHCO_3$, Na_2HPO_4 or Na_2SO_4. (g, h) The *ΔI vs. v* plots used for the determination of C_s, C_{dl} and ECSA at 0.7 V *vs.* RHE.

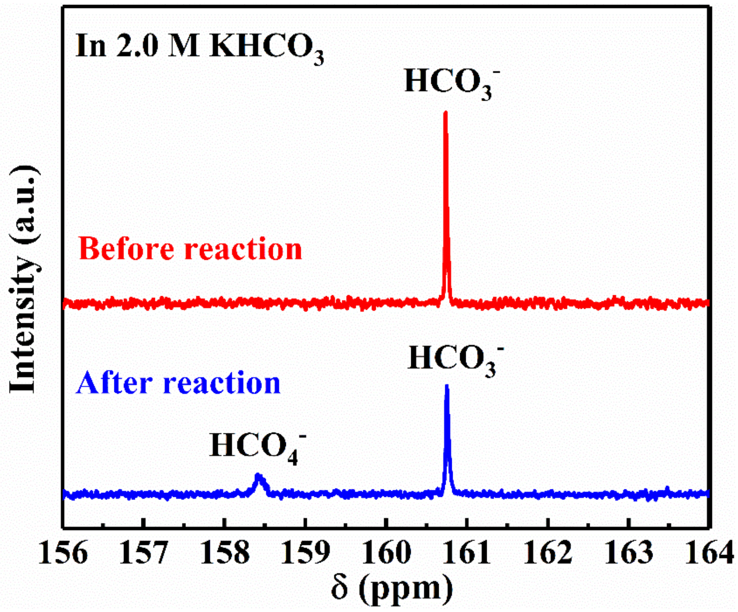

Fig. S4 The ^{13}C NMR signals of HCO$_3^-$ and HCO$_4^-$ in the KHCO$_3$ electrolyte after 25 min of reaction at 3.0 V *vs.* RHE.

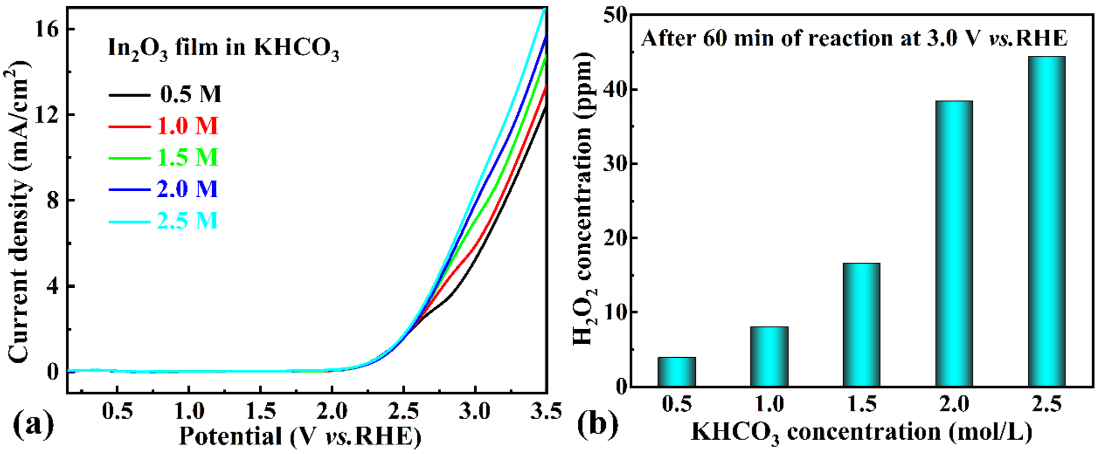

Fig. S5 (a) The LSV curves and (b) the production amount of H_2O_2 for the In_2O_3 film electrode in $KHCO_3$ electrolyte with different concentrations.

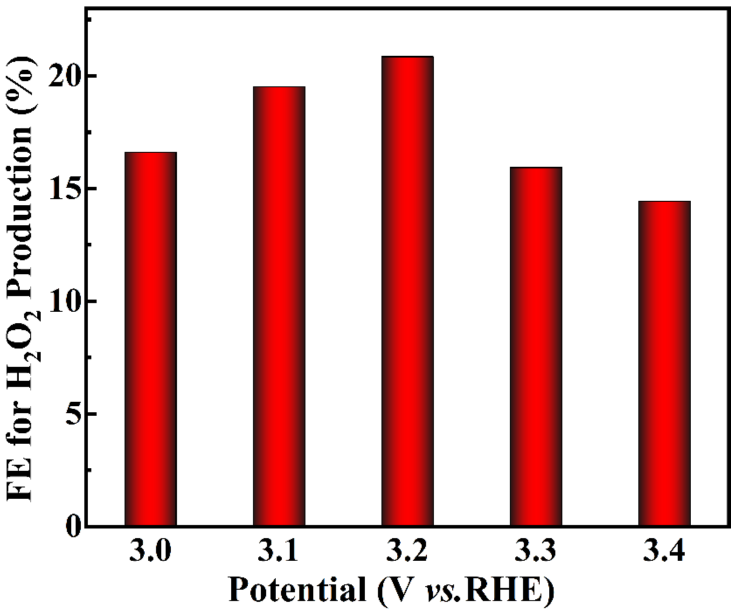

Fig. S6 The Faraday efficiency of H_2O_2 production in the cell with 2.0 M $KHCO_3$ electrolyte and In_2O_3 film anode.

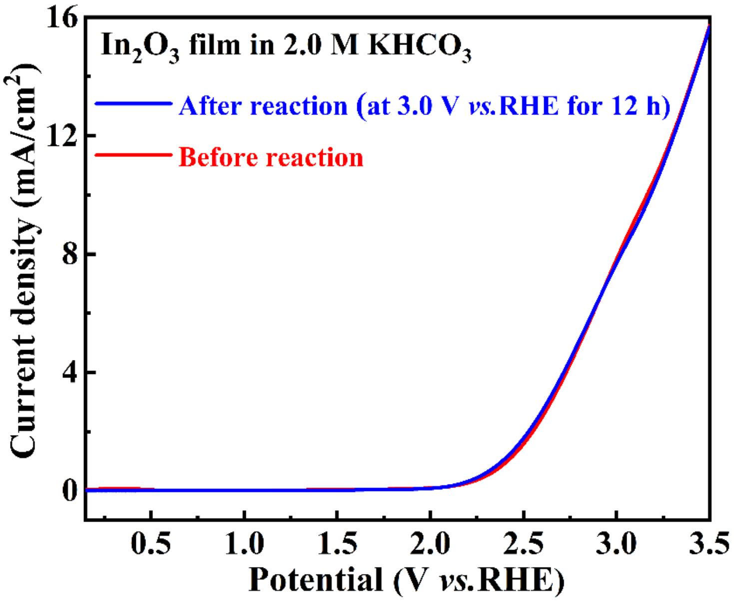

Fig. S7 The contrastive LSV for the same In_2O_3 film electrode before and after 12 h of reaction in 2.0 M $KHCO_3$ electrolyte at 3.0 V *vs.* RHE.

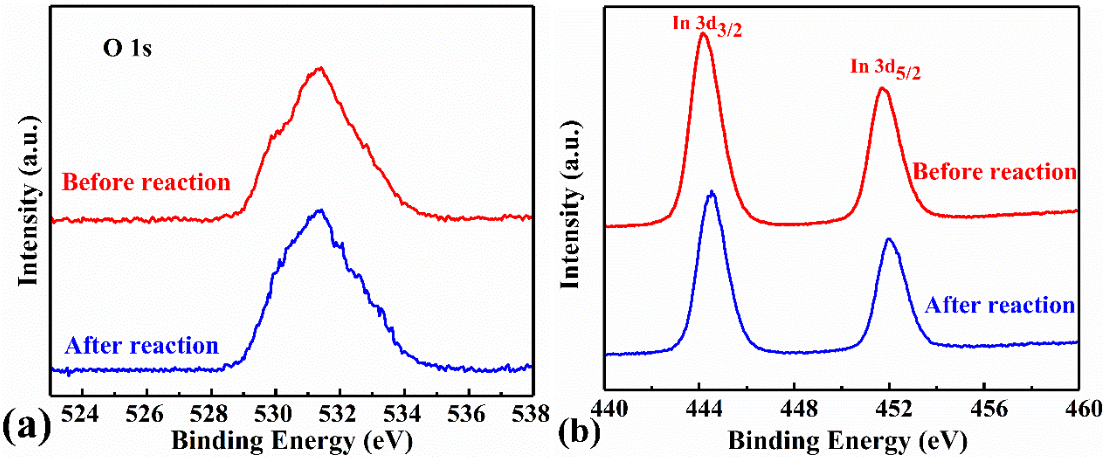

Fig. S8 (a) O 1s and (b) In 3d XPS spectra of the In_2O_3 film electrode before and after 12 h of reaction in 2.0 M $KHCO_3$ electrolyte at 3.0 V *vs.* RHE.

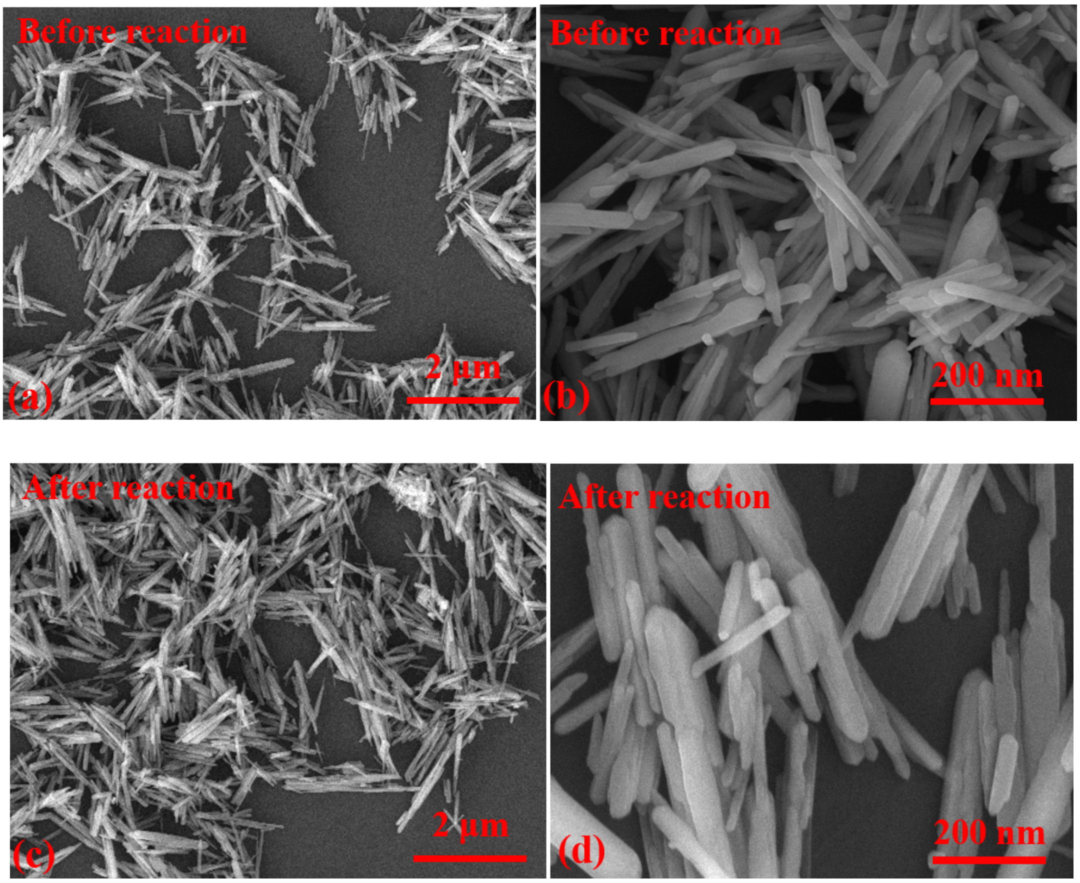

Fig. S9 The SEM images of MnO_2 powders (a, b) before and (c, d) after 12 h of reaction in $KHCO_3$ electrolyte.

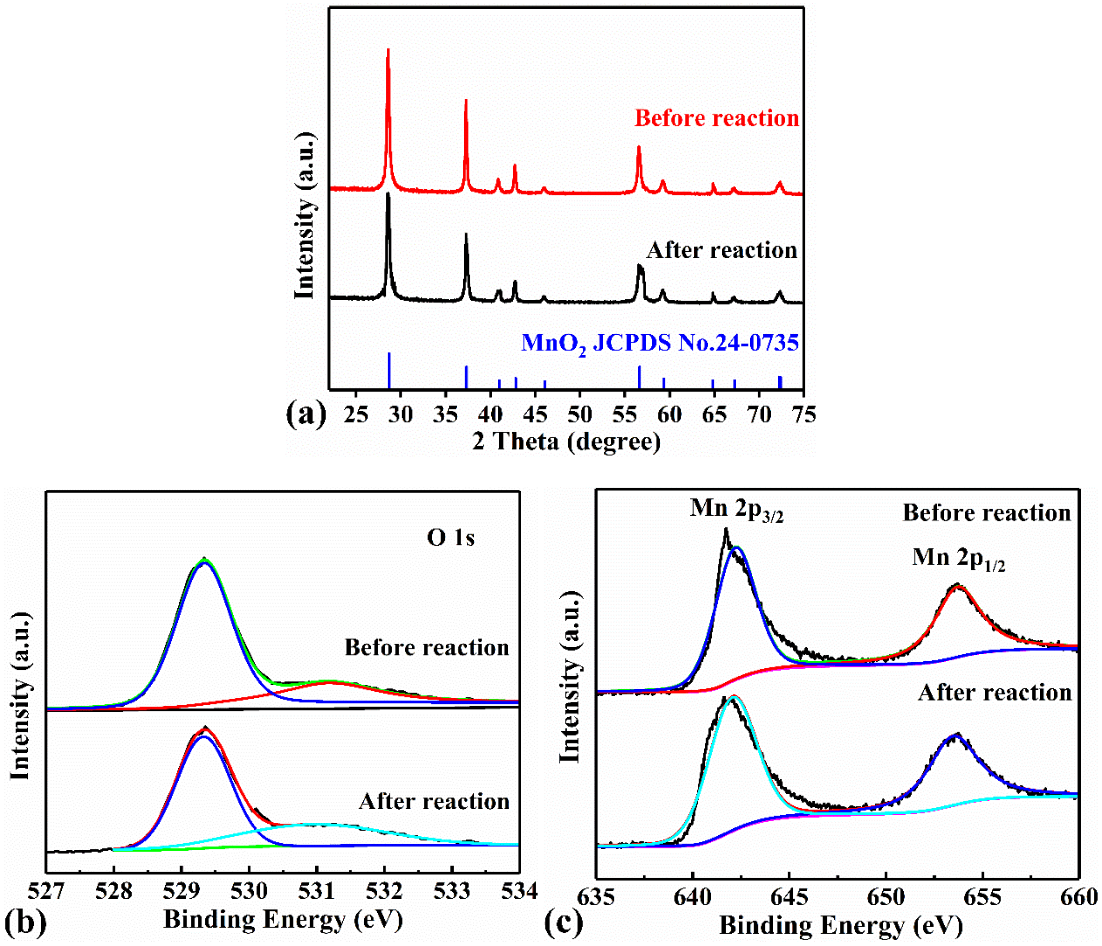

Fig. S10 (a) XRD patterns, (b) O 1s and (c) Mn 2p XPS spectra of MnO_2 powders before and after 12 h of reaction in $KHCO_3$ electrolyte.

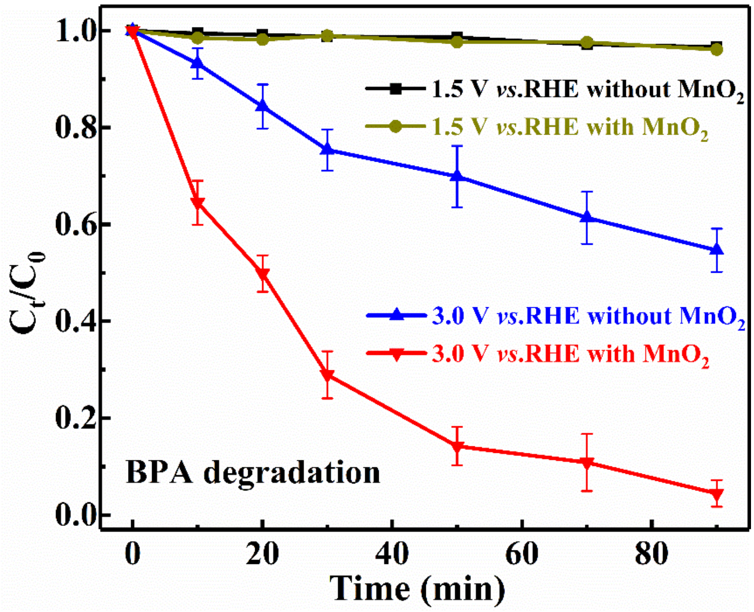

Fig. S11 The degradation curves of 10 ppm BPA in 2.0 M $KHCO_3$ electrolyte with 0.6 g/L MnO_2 and without MnO_2 powders.

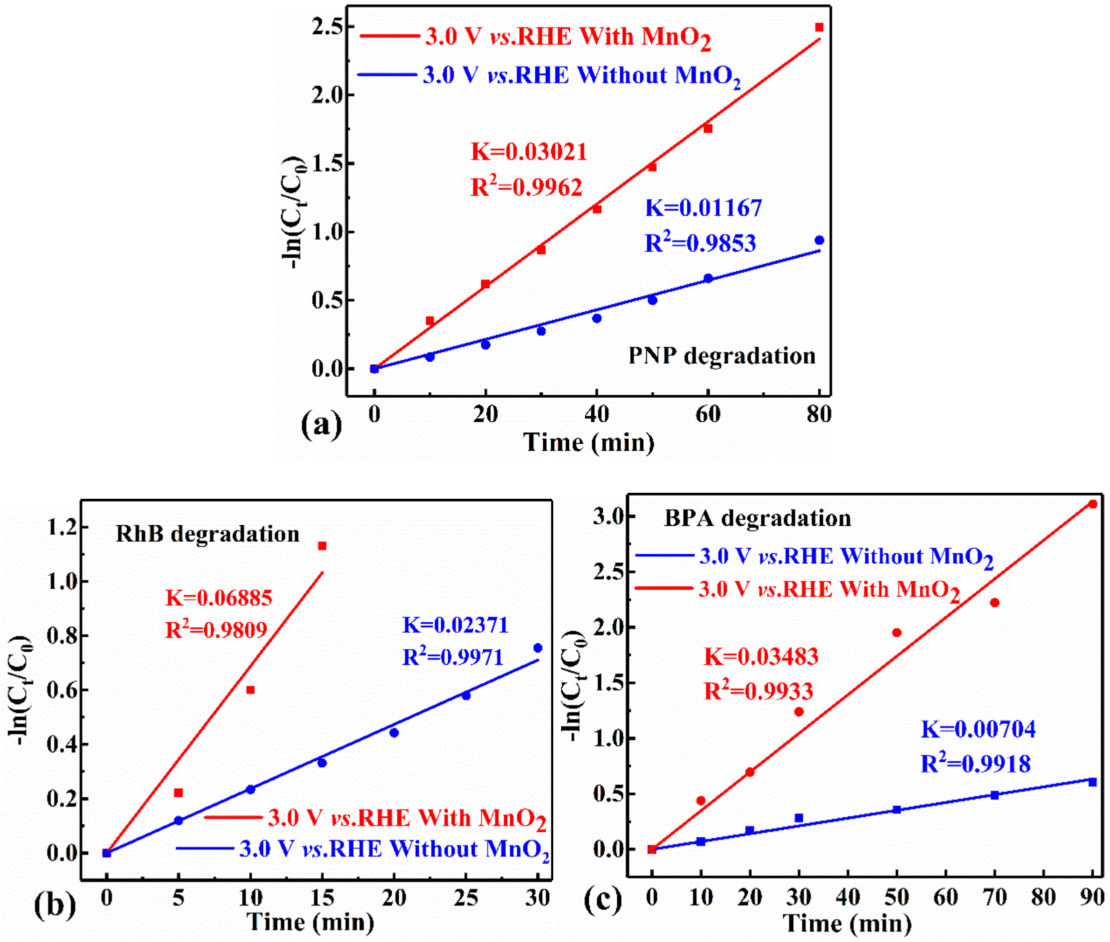

Fig. S12 The pseudo-first-order kinetic curve of the degradation of (a) PNP, (b) RhB and (c) BPA in the In_2O_3 film electrode-based cell with MnO_2 powders-containing $KHCO_3$ electrolyte.

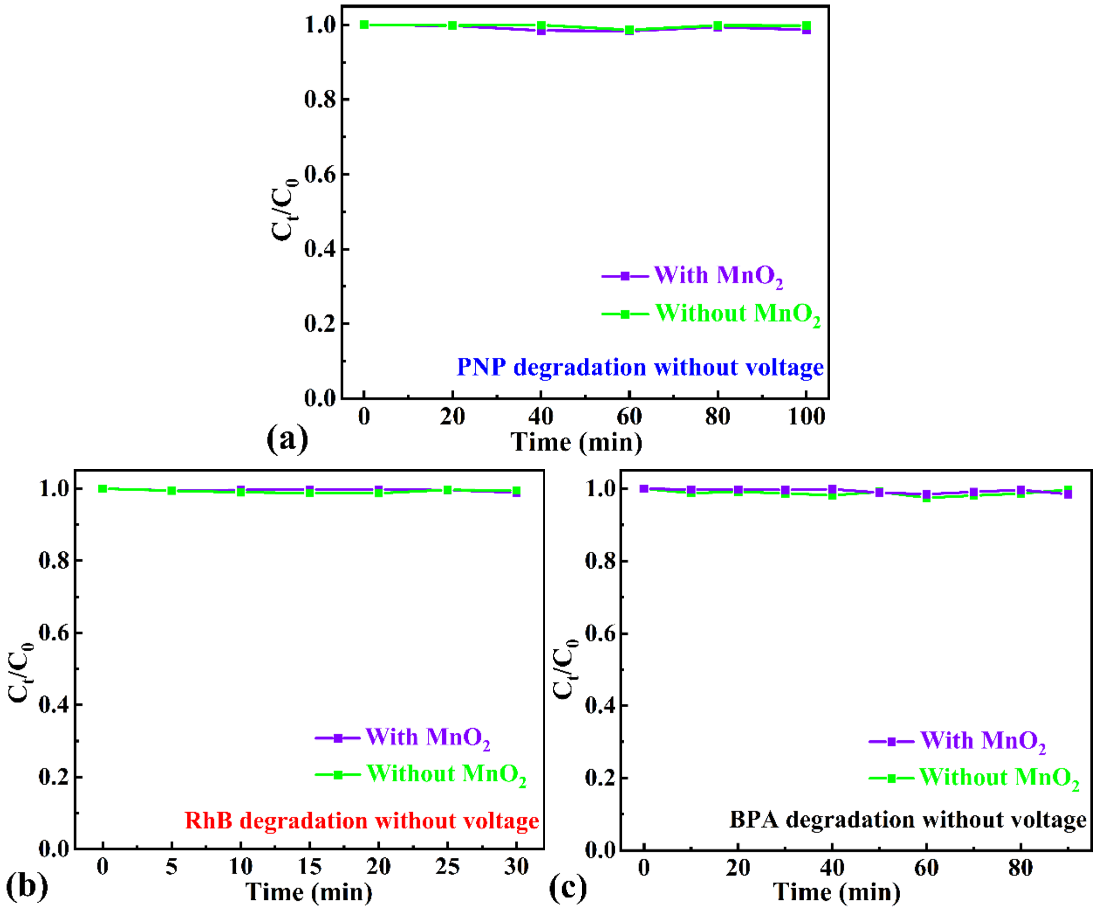

Fig. S13 The degradation of (a) 10 ppm PNP, (b) 10 ppm RhB and (c) 10 ppm BPA in 2.0 M $KHCO_3$ aqueous solution (voltage-free) with and without 0.6 g/L MnO_2 powders.

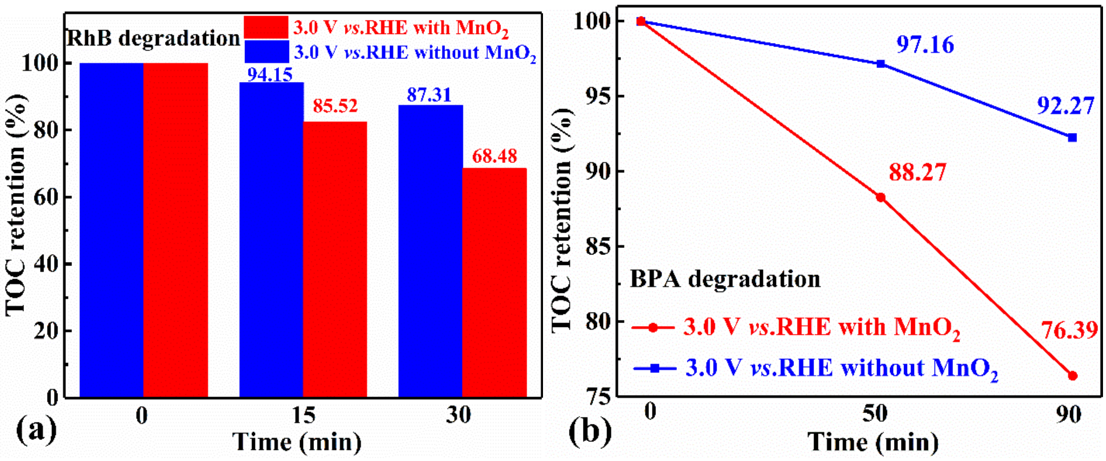

Fig. S14 The TOC retention rate of (a) 10 ppm RhB and (b) 10 ppm BPA *vs.* reaction time in 2.0 M $KHCO_3$ electrolyte with and without 0.6 g/L MnO_2 powders at 3.0 V *vs.* RHE.

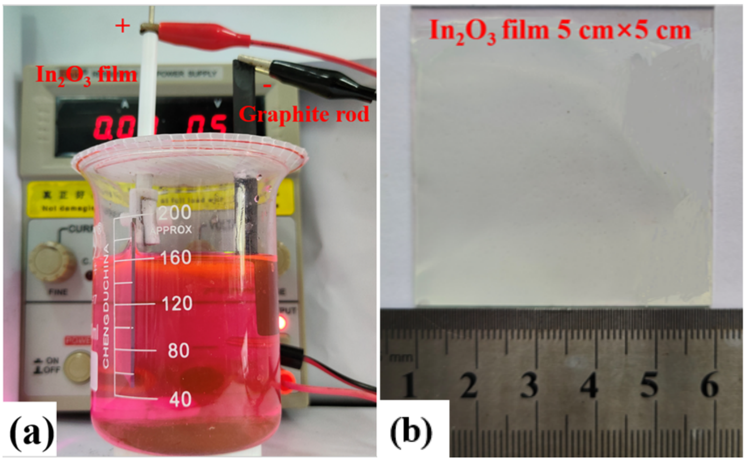

Fig. S15 (a) The scale-up two-electrode cell for the degradation of 10 ppm RhB, (b) the photograph of In_2O_3 film.

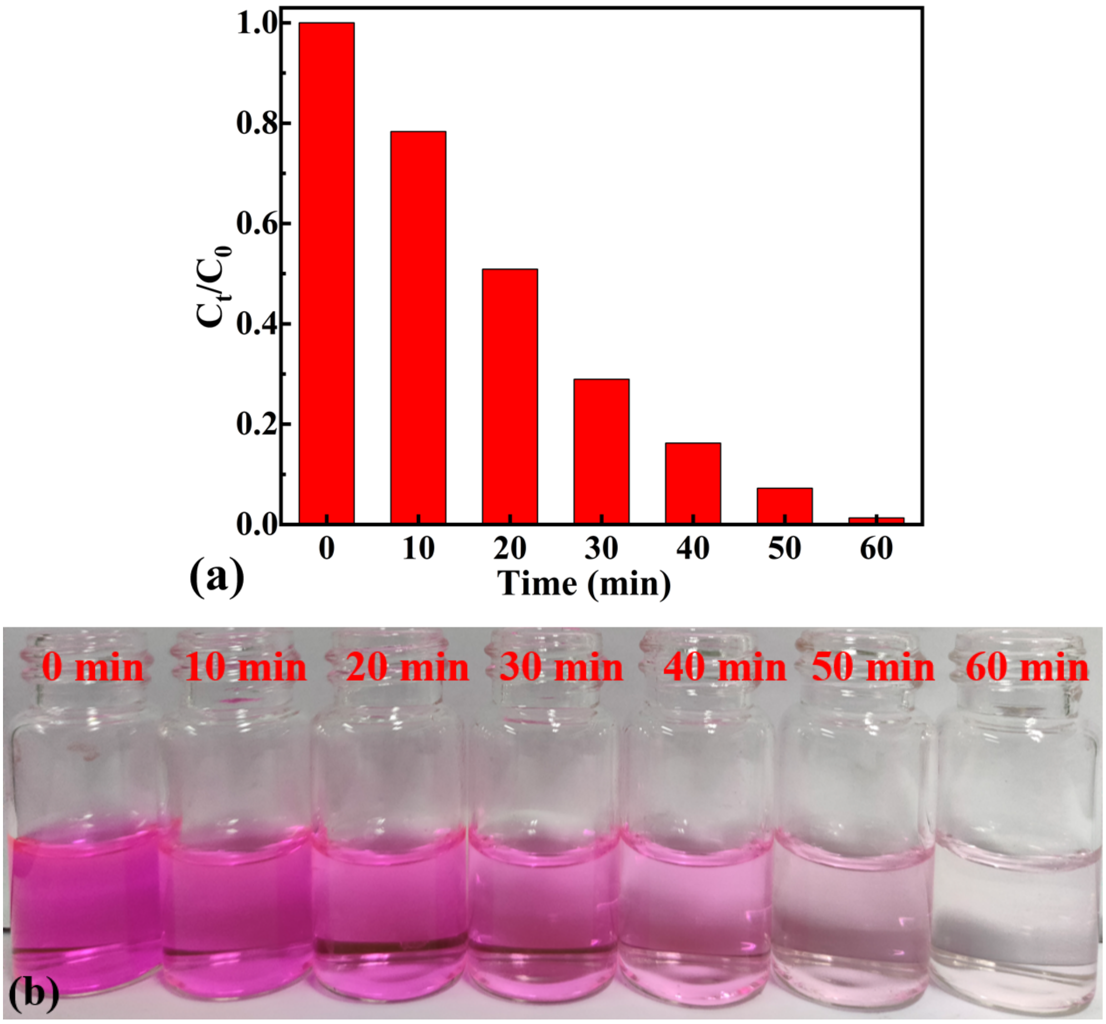

Fig. S16 (a) The degradation rate and (b) photograph of 150 mL of 10 ppm RhB through the two-electrode cell with a 5.0 V of DC voltage.

Table S1 The ICP detected content of dissolved In and Mn ions in the $KHCO_3$ electrolyte after 12 h of reaction at 3.0 V *vs.* RHE.

Condition	In ion/ppm	Mn ion/ppm
Before reaction	0	0
After reaction	0.081	0.362

Reference.

1 T. Waitz, T. Wagner, T. Sauerwald, C. D. Kohl and M. Tiemann, *Adv. Funct. Mater*, 2009, **19**, 653-6

2 Y. Wu, L. Yang, B. Wu, J. Li, B. Liu, G. Ke, F. Dong, Y. Zhou and H. He, *Catal. Lett*, 2020, **151**, 901-908.